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THERMODYNAMICS

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After several meetings, this first Editorial Advisory Board submitted its report to the McGraw-Hill Book Company in September, 1925. In it were detailed specifications for a correlated series of more than a dozen texts and reference books which ha since become the McGraw-Hill Series in Chemical Engineering.

Since its origin the Editorial Advisory Board has been benefited by the guidance and continuing interest of such other distinguished chemical engineers as Manson Benedict, John R. Callaham, Arthur W. Hixson, H. Fraser Johnstone, Webster N. Jones, Paul D. V. Manning, Albert E. Marshall, Charles M. A. Stine, Edward R. Weidlein, and Walter G. Whitman. No small measure of credit is due not only to the pioneering members of the original board but also to those engineering educators and industrialists who have succeeded them in the task of building a permanent literature for the chemical engineering profession.

THE SERIES

Chemical Engineering Thermodynamics

BY

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INTERNATIONAL STUDENT EDITION

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CHEMICAL ENGINEERING THERMODYNAMICS

INTERNATIONAL STUDENT EDITION

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To my wife

CONSTANCE WOODBURY DODGE,

who writes more exciting books

PREFACE

One may reasonably ask, "Why another book on thermodynamics; are there not more than enough on this subject now?" Thermodynamics is a method of attack on problems, a versatile tool of broad applicability. It finds many applications in the fields of physics, chemistry, and mechanical and chemical engineering and limited application·in other fields. Frequently in a given university there may be as many as three or even four courses in thermodynamics, each offered by a different department. Administrative officers of colleges find this difficult to understand but there is a legitimate reason for the apparent duplication of effort. Admittedly the fundamentals are the same for all fields, but the applications and viewpoints are different. Long experience in the teaching of thermodynamics to college students has only confirmed a conviction of long standing that the vast majority of students best learn the fundamentals as the author learned them, through application to concrete, practical problems. The fundamentals are too abstract, too broad in their implication to be grasped by any other process.

Then, too, the question of motivation of interest must not be overlooked. The average engineering student is a very pragmatic individual. Perhaps educators should deplore this, but the fact remains. He is apt to be impatient with abstract ideas or theories and will lose interest quickly unless their value as useful tools can be continually brought home to him by applications in his own field which he recognizes as being practical.

This, then, is the author's excuse for another book on thermodynamics. The many important applications in the field of chemical engineering amply justify it. When this book was started there was no text dealing specifically with the applications of thermodynamics to chemical engineering problems but since then at least one book has appeared that deals exclusively with the subject and a few others that treat it briefly along with other topics. There is room, the author believes, for at least one more.

The present book is an outgrowth of a graduate course started at Yale over 15 years ago. Although intended primarily for graduate students, the book should also be useful as an undergraduate text as it assumes no previous knowledge of thermodynamics and develops each topic from fundamentals that are in the curriculum of the first three years of any good undergraduate course in chemical engineering. It is essential to do

this even for a graduate course because beginning graduate students have different backgrounds and some will have had no real exposure to thermodynamics. Even those who have had a good undergraduate course will find a certain amount of repetition advantageous.

The plan of the present book is believed to be unique in at least a few respects. The first two chapters are devoted to developing the fundamental concepts and definitions and especially the ideas underlying the two great laws of thermodynamics. This is purposely done with a minimum use of advanced mathematics. Once the concepts are presented, their development into usable tools becomes a purely mathematical problem, and this is the method of approach adopted in Chap. III. This first mathematical development is restricted to a very simple type of system. The next logical step was to extend the development to more complex systems, and that is the business of Chap. IV. The underlying idea of this chapter is to develop, with the aid of the calculus, the concepts of the two laws into general equations of equilibrium from which the many special equations emerge almost automatically when the special conditions are inserted. These equations are commonly developed in somewhat unrelated fashion in separate chapters. There are advantages in showing their interrelation in this way. But there is one disadvantage, too, and that is the deadly dryness of a chapter bristling with mathematical formulas, unleavened by any interesting applications. Most teachers will probably elect to do as the author does—skip this chapter and get along to more interesting things but recognizing that it is a useful storehouse of relationships that can be referred to later when need arises.

After developing differential equations relating thermodynamic properties to the variables of state, the equations must be integrated. This requires *pvt* data, and so the next logical step is to review such data and the equations of state for expressing them. That is the task of Chap. V. Chapter VI then brings the differential equations and the means for integrating them together and develops the numerical calculation of the thermodynamic properties.

The first six chapters have laid the foundations for the applications to specific operations and processes that constitute the subject matter of the remaining seven chapters. It is easy to quarrel about the choice of the applications. The author makes no claim that his choice is the best one; he has merely chosen those that happened to interest him the most and which he had developed through his own experience. Many important ones are missing which he would have liked to include but which limitations of time and space forbade.

The dominating idea that the author has continuously striven to develop is that thermodynamics should be a useful tool to a chemical

engineer, and this must be continually demonstrated by solving short, specific problems of the type likely to be encountered in dealing with the broader problems that arise in practice. Though falling far short of the ideal in this respect, a step in this direction has been taken by the inclusion of 135 solved illustrations. These are the real meat of the book and the effort behind it will have been worth while if these illustrations suggest to the reader ways in which problems encountered in his own experience may be attacked.

Many persons have contributed indirectly to the book by helping to form the author's ideas, but there is no adequate way for him to repay this debt except through a general acknowledgment. Where material has been taken from the publications of others or from manufacturer's catalogues, acknowledgment has been made in the text. A particular debt of gratitude is due the several generations of graduate students who through classroom discussions and solution of problems have done much to shape the entire course of the book. The author wishes particularly to acknowledge an indebtedness to his colleague, Dr. Harding Bliss, who has critically read much of the manuscript and offered many valuable suggestions that have been incorporated in the text. Finally, the author wishes to acknowledge a debt of long standing to Harvey N. Davis, formerly Professor of Mechanical Engineering at Harvard University, more recently President of Stevens Institute of Technology, and at present Director of the Office of Production Research and Development of the WPB, who introduced him to the subject of thermodynamics and aroused the interest which has resulted in this book.

<div align="right">Barnett F. Dodge.</div>

New Haven, Conn.,
   April, 1944.

CONTENTS

LIST OF SYMBOLS

1. Capitals

A Work function $(E - TS)$ per unit mass or per mole*
Empirical constant
Area in general

Amagat compressibility factor $\dfrac{pv}{p_1v_1}$

Component in a reaction

B Empirical constant
Component in a reaction
Availability

C Molal heat capacity ($\bar{C}$ refers to mean heat capacity or to partial heat capacity)
Empirical constant

Compressibility factor $\dfrac{pv}{RT}$

Discharge coefficient in fluid flow
   C_o = hydraulic coefficient
   C_a = adiabatic coefficient
   C_m = coefficient based on mean density
Concentration, moles per liter
Component in a reaction
Integration constant

D Diameter
Empirical constant
Degrees of freedom
Component in a reaction
Moles of distillate

E Electromotive force (e.m.f.)
Empirical constant
Energy content per unit mass or per mole*
Over-all fractionation factor or enrichment ratio (distillation)

F Free energy $(H - TS)$ per unit mass or per mole*

Force, total load
Energy dissipated by friction
Empirical constant
Moles of feed in a distillation process

G General thermodynamic property per unit mass or per mole*
Mass velocity, pounds per unit of time per unit of area

$\bar{G}$ Partial mass-value or molal value of the property $= \dfrac{\partial \mathbf{G}}{\partial N_i}$ or $\dfrac{\partial \mathbf{G}}{\partial m_i}$
where N_i = number of moles of any component and m_i = mass of any component.

Thus we may have $\bar{F}_i = \dfrac{\partial \mathbf{F}}{\partial N_i}$,

$\bar{v}_i = \dfrac{\partial V}{\partial N_i}$, $\bar{C}_{p_i} = \dfrac{\partial C_p}{\partial N_i}$, etc.

H Enthalpy per unit mass or per mole* (used for enthalpy of a vapor in discussions where it is desirable to distinguish between the enthalpy of a vapor and that of a liquid)

H_p Height of packing in a packed tower

I Integration constant
Electrical current
Intensity of magnetization
Enthalpy of a mixture of liquid and vapor

J Mechanical equivalent of heat
Intensity of visible radiation

K Equilibrium constant in chemical reaction (with various subscripts)
   K_a Equilibrium constant in terms of activities

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* The total value of any extensive property except volume will be denoted by the symbol in bold-face type.

K_c Equilibrium constant in terms of concentrations

K_f Equilibrium constant in terms of fugacities

K_p Equilibrium constant in terms of partial pressures

K_p° Limiting value of K_p as $p \rightarrow 0$

K_x Equilibrium constant in terms of mole fractions

K_γ Equilibrium constant in terms of activity coefficients $= \dfrac{K_f}{K_p}$

Kinetic energy

Equilibrium ratio in liquid-vapor phase equilibrium $= \dfrac{y}{x}$

Characterization factor for petroleum products

Integration constant

L Length or distance

Moles of liquid in a distillation process

Latent heat of vaporization per mole (or per unit mass)

Component in a reaction

M Molecular weight

Component in a reaction

N Number of moles

Number of components

O Moles of overflow liquid in a tower

P Power (work per unit time)

Q Quantity of heat

Quantity of electricity or electrical charge

R Gas constant

Thermal resistance

Fluid meter reading (with subscript)

Reflux ratio

Re Reynolds number

S Entropy per unit mass or mole*

Surface area in special cases

T Thermodynamic temperature in general, °R. or °K.

T_B Boiling point on thermodynamic scale

T_F Freezing point on thermodynamic scale

U Over-all coefficient of heat transfer

V Total volume

Moles of vapor in a distillation process

W Work in general

Moles of bottom product in a distillation process

W_o Shaft work

X Mole ratio in liquid phase

Y Mole ratio in vapor phase

Expansion factor in fluid flow

Z Number of phases

2. Lower Case

a Empirical constant

Activity ($\bar{a}$ for component in a solution)

Surface of packing per unit volume

Stoichiometric number

b Empirical coefficient

Stoichiometric number

Stefan-Boltzmann law constant

c Empirical coefficient

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* The total value of any extensive property except volume will be denoted by the symbol in boldface type.

Volume concentration
Velocity of light
Conventional chemical constant
Clearance in a compressor
Specific heat

d Differential operator

e Base of natural logarithms
Efficiency
Empirical constant
Stoichiometric number

f Fugacity ($\bar{f}$ for fugacity of component of a solution)
Friction factor in Fanning equation
Correction factor
Fraction of a flowing fluid taking one branch at a division point

g Acceleration of gravity

h Film coefficient of heat transfer
Fluid head
Enthalpy of a liquid (in discussions where it is desirable to distinguish between the enthalpy of a vapor and that of a liquid)

i Chemical constant
Constant of integration

k Thermal conductivity
Ratio of specific heats
Empirical constant
Henry's law constant

l Stoichiometric number
Empirical constant
Fraction of liquid in feed to rectifying column

m Mean hydraulic radius
Molality
Mass
Stoichiometric number
Slope of an operating line

n General exponent
Revolutions per unit time
Molal rate of flow

Empirical constant
Number of stages in compression
Exponent in polytropic expansion or compression
Number of steps or transfer units in a tower

p Pressure in general; total pressure
Vapor pressure when used with subscript

$\bar{p}$ Partial pressure when used with subscript

q Quantity of heat transferred per unit time
Volume rate of flow
Heat quantities in distillation (with various subscripts) per unit quantity of some stream
A ratio of heat quantities, used in rectification theory
Heats of solution

r Radius
Weight fraction
Ratio of pressures in expansion or compression
Ratio of stoichiometric numbers

t Temperature (other than absolute or thermodynamic)

u Linear velocity

v Specific volume or molal volume

w Mass rate of flow

x Mole fraction in general
Mole fraction in liquid phase
General independent variable
Quality of a vapor

y Mole fraction in gas phase
General independent variable

z Height above a datum level
Mole fraction of component in a mixed (*i.e.*, liquid and vapor) feed to a rectifying column

3. Greek Letters

α (Alpha) Empirical constant
Relative volatility in liquid-vapor equilibria
The volume residual quantity $\dfrac{RT}{p} - v$

β (Beta) Empirical constant
Ratio of diameters of throat to pipe in a head meter
Coefficient of performance of a refrigerating machine

γ (Gamma) Empirical constant
Fugacity or activity coefficient = $\dfrac{f}{p}$ or $\dfrac{a}{x}$

Δ (Delta) Finite difference
Residual quantity

δ (Delta) Empirical constant

ϵ (Epsilon) Exponent in adiabatic compression
Intensity of total radiation

ζ (Zeta) Generalized force
Fraction vaporized or condensed
Fraction converted in a chemical reaction

H (Eta) Magnetic-field strength

θ (Theta) Time
Temperature on ideal gas scale
A characteristic temperature

κ (Kappa) Compressibility $= \dfrac{1}{v}\dfrac{\partial v}{\partial p}$
κ_S for adiabatic compressibility
κ_T for isothermal compressibility

λ (Lambda) Wave length
Latent heat of phase change (in general)
Latent heat of vaporization per unit mass (Chap. XIII only)

μ (Mu) Joule-Thomson coefficient
Absolute viscosity
Chemical potential

π (Pi) Ratio of circumference to diameter of circle
Special function of p, v, and T which $= \dfrac{1}{RT}\int v\,dp$ $\pi_0 = \dfrac{1}{RT}\int_{p^o}^{p} v\,dp$

ρ (Rho) Density

Σ (Sigma) Summation of

Σn Summation of stoichiometric numbers of a chemical reaction $= l + m + \cdots - a - b - \cdots$

σ (Sigma) Surface tension

ϕ (Phi) Function of

X (Chi) Generalized displacement

χ (Chi) Function of
Magnetic susceptibility

ψ (Psi) Function of

4. Subscripts
(Only those having general use)

$A, B, C, \ldots N$ Refer to components

B Refers to boiling point or to boiler in a rectifying column

C Refers to critical state or condenser in a rectifying column or to a condensation process

D Refers to distillate or overhead product from a distillation process

E Refers to an expander or exhausting section of a rectifying column

F Refers to freezing point or feed to a distillation process

L Refers to liquid phase or to heat leak to a low-temperature system

R Refers to a reduced state, *i.e.*, a state relative to the critical state
Refers to auxiliary refrigeration system

V Refers to vapor phase or to a vaporization process

i, j Refer to any component or to a point of intersection of operating lines

m Refers to a mean value, to a mixture, or to exhausting section of a rectifying column

n Refers to enriching section of a rectifying column

p, v, T Refer to constant volume, pressure, or temperature. Similarly for other properties such as S, H, or E

s Refers to standard reference condition for gas volume, to a saturated phase, or to a solution

t Refers to a tangent line

W Refers to bottom product from a rectifying column

$0, 1, 2, \ldots$ Refer to different states or to different points in a process or are used to differentiate constants having the same symbol. 0 usually refers to a standard state or to the ice point or to absolute zero or to the lowest temperature in the surroundings at which large amounts of heat may be rejected

5. Superscripts

$°$ Refers to standard state of low pressure where gases are ideal

∞ Refers to state of infinite dilution

$*$ Refers to equilibrium state

$', '', \ldots, z$ Refer to different phases. More specifically, $[']$ refers to a liquid phase and $['']$ to a vapor phase

6. Abbreviations and Special Conventions

ln natural logarithm

log logarithm to base 10

(g), (l), (s)	Refer to state (gas, liquid, or solid) of substance in writing a chemical reaction
$\rightarrow$	approaches in value
hp.	horsepower
hp.-hr.	horsepower-hour
kw.	kilowatt
kw.-hr.	kilowatt-hour
cu. ft. per min.	cubic feet per minute
∂	partial differential operator
lb. per sq. in.	pound per square inch
lb. per sq. in. abs.	pound per square inch absolute
°C.	degree on centigrade scale
°F.	degree on Fahrenheit scale
°K.	degree on Kelvin scale

°R.	degree on Rankine scale
cu. ft.	cubic foot
e.m.f.	electromotive force
B.t.u.	British thermal unit
c.h.u.	centigrade heat unit
H.E.T.P.	height equivalent to a theoretical plate
H.T.U.	height of a transfer unit
ft. lb.	foot-pound
c.c.	cubic centimeter
r.p.m.	revolution per minute
—	bar over an extensive property denotes a partial quantity. See under G in section 1
Aq.	refers to a dilute solution of no definite concentration. Frequently a 1-molal solution is implied.

CHEMICAL ENGINEERING THERMODYNAMICS

CHAPTER I

DEFINITIONS AND FUNDAMENTAL CONCEPTS

SCOPE OF CHEMICAL ENGINEERING THERMODYNAMICS

The science of thermodynamics may be said (broadly speaking) to deal with (1) energy and its transformations and (2) tendency to change and equilibria with particular reference to systems involving thermal effects. This is merely a convenient way of classifying all the applications of thermodynamics and indicates how broad a field it serves. "Pure" thermodynamics is based on two fundamental laws. These laws were developed and extensively tested in the latter half of the nineteenth century and may be said to rest on a very broad foundation of experience. A third law has been developed during the present century; but although of a fundamental character and based on sound experimental and theoretical grounds, it has nothing like the scope of application of the other two laws. Its chief application is in the field of chemical equilibrium, and it will be treated briefly in the chapter devoted to that subject. It is sufficient for our present purpose to note that, whereas the first two laws led to the definition of new and useful functions, the third law, in essence, merely limits the value of one of these functions (the entropy).

Practically all thermodynamics, in the ordinary meaning of the term, is "applied thermodynamics" in that it is essentially the application of these three laws, coupled with certain facts and principles of mathematics, physics, and chemistry, to problems in various fields of science and engineering. The fundamental laws are of such generality that it is not surprising that the science of thermodynamics finds extensive application in physics, chemistry, mechanical engineering, and chemical engineering.

For purposes of instruction the field of chemical engineering is commonly subdivided into a number of unit operations, mainly physical in character, such as heat transfer, fluid flow, evaporation, and filtration, and various unit processes, involving combination of these physical operations with chemical changes, such as catalysis, nitration, and esterification. The study of all these operations and processes may be

approached from three essentially different viewpoints, which may be roughly classified as follows:

1. Limiting conditions of operation and energy quantities involved.
2. Rate of transfer of energy or material.
3. Equipment, materials, mechanism, etc.

Chemical engineering thermodynamics deals with only the first of these categories.

Let us take a concrete illustration from the field of distillation. Thermodynamics is concerned with the limiting or maximum degree of separation that can be achieved in distillation under given conditions of pressure, temperature, and composition of the system, *regardless of the particular mechanism employed.* In other words, it is primarily concerned with the equilibrium relationships governing the particular system being distilled and with the limiting energy requirements. The main purpose of the application is to set up ideal standards by comparison with which the performance of an actual and imperfect mechanism can be judged. The details of the actual application of thermodynamics to obtain the limiting conditions might not differ from those used in the field of chemical thermodynamics. Thus one would be concerned with phase equilibrium relationships, with vapor pressures, latent heats of vaporization, etc.— topics commonly considered to be in this field. The real difference, and an important one, is in viewpoint. In the case of chemical engineering thermodynamics, the whole treatment focuses upon the application to some engineering problem, and this may modify the details in many ways. It may, for example, cause a considerable shift in emphasis so that points which seem of the greatest importance from the standpoint of pure theory may become decidedly secondary and even of minor importance from the viewpoint of practical application. Furthermore, chemical engineering thermodynamics generally goes a step further and, after establishing the limiting conditions, considers the degree of approach of practical equipment to the ideal limits—considers efficiencies, in other words—and possible improvements to allow a closer approach.

The relation between thermodynamics and rate of change is a question that causes some confusion of thought and hence is worth a brief discussion. The rate of any process is, in general, determined by a driving force and a resistance. Thermodynamics can contribute to the determination of the driving force but can tell nothing about the resistances. Consequently, one cannot make predictions about rate of change from thermodynamics alone. For example, in the case of a chemical reaction, with the aid of thermodynamics one can determine the maximum possible yield under a given set of conditions, given infinite time for the reaction to take place, but the actual rate at which the reaction will proceed toward that yield is outside the scope of thermodynamics. Likewise. in

such unit operations as heat transfer or gas absorption, thermodynamics is applicable to the determination of the driving force for the change, of the energy requirements, of the minimum amount of absorbing liquid necessary, and of related quantities; but the rate of transfer also involves resistances of fluids and of solids to the flow of heat or material, and these introduce questions of mechanism that are foreign to thermodynamics.

TEMPERATURE

Qualitative Concepts.—Temperature is probably the most important single variable used in all thermodynamic discussions, and hence it is essential to gain at the outset as clear a conception as possible of its significance. Unlike pressure, another important variable, it cannot be measured in terms of simple, fundamental quantities but must be measured quite indirectly and the interpretation of these measurements into something that has an absolute significance involves many complications. For many practical purposes, temperature is best regarded as the driving force for heat energy. One body is at a higher temperature than another if heat will flow from the first to the second. When equilibrium is established and no transfer occurs when the two bodies are placed in juxtaposition, the two bodies are at the same temperature. The whole measurement of temperature is based on the assumption that all substances placed in contact and remaining static will eventually come to thermal equilibrium and be at the same temperature.

From the kinetic rather than the thermodynamic point of view, temperature is related to the kinetic energy of the molecules. The kinetic theory of gases tells us that the molecules in a given substance are in rapid translational motion and with greatly varying speeds. Temperature is therefore a statistical quantity related to the average speed.

Quantitative Definition.—A quantitative definition of temperature may be based on any property of substances that changes with temperature, such as thermal expansion, electrical resistance, contact electromotive force (e.m.f.), or vapor pressure. To establish a numerical scale of temperature, it is first necessary to define the length of a degree. This is commonly done by choosing a fixed and readily reproducible interval of temperature such as that between the freezing point and boiling point of pure water at the standard atmospheric pressure and dividing this fundamental interval into an arbitrary number of degrees (100° in the case of the centigrade scale and 180° for the Fahrenheit scale). The choice of the zero point is also a purely arbitrary matter. Any other temperature is then defined by the following simple equation applying specifically to the centigrade scale:

$$t = \frac{100(G - G_0)}{G_{100} - G_0} \tag{I.1}$$

where t = any temperature on a centigrade scale.

G = value of the given property at the temperature t.

G_0 and G_{100} = values of the property at 0 and 100°, respectively.

This equation merely assumes the simplest possible relationship—a linear one—between the property of a substance and its temperature.   There would be no point in (and no basis for) assuming any more complex relationship.   The properties most commonly used for the industrial measurement and control of temperatures are

1. Volume expansion of gases, liquids, and solids at constant pressure.
2. Pressure increase of liquids and gases at constant volume.
3. Vapor pressure of liquids.
4. Electrical resistance of metals (particularly platinum).
5. E.m.f. at the junction of two dissimilar metals.

It should be clear from the definition of temperature by Eq. (I.1) that no two scales so defined will agree at any temperatures other than the two fundamental ones of 0 and 100°.   Table I.1 illustrates this fact, which is of fundamental importance.

TABLE I.1.—DISAGREEMENT OF TEMPERATURE SCALES BASED ON PROPERTIES OF SUBSTANCES

Property	Reading at following temperatures, °C., on the thermodynamic scale:	
	50°	200°
Expansion of mercury*........................	50.0	202.2
Vapor pressure of ethyl alcohol................	23.3	1320
E.m.f. of platinum, platinum-rhodium couple...	46.4	222.5
Platinum resistance...........................	50.25	195.7

* Expansion of container neglected.

The calculations were made by Eq. (I.1), using data obtained from the International Critical Tables.

Of course, the further one gets from the fundamental interval, the larger the deviations become, in general.   If a gas like hydrogen or nitrogen is used as the working substance, the corrections to the absolute scale are much less.   For example, at -200 and $+200°$C. the corrections to the constant-volume hydrogen scale are only $+0.06$ and $+0.02°$, respectively. At 1000°C. the constant-volume nitrogen scale has a correction of $+0.7°$C.

The Absolute Scale.—It would clearly be of great advantage to have a scale that is independent of the properties of any particular substance, *i.e.*, an absolute scale.   The second law of thermodynamics, as will be shown later, furnishes the basis for an absolute scale and also permits the

definition of a zero point, or "absolute zero" as it is commonly called. No "absolute thermometer" can be constructed, but it is possible from the laws of thermodynamics to calculate the corrections to be applied to the readings of a practical thermometer to convert them to the absolute scale. This process of "establishing" the absolute temperature scale is done by such institutions as the National Bureau of Standards in this country and similar national standardizing laboratories in other countries. The thermometers generally used to establish this scale are gas thermometers using helium, hydrogen, or nitrogen as the thermometric substance.

A temperature scale that is absolute (*i.e.*, independent of the properties of any individual substance) may be based on the use of an ideal gas as the thermometric fluid, and this is often referred to as the "ideal-gas temperature scale." Since there is actually no ideal gas, this is not a practical scale, but its importance is in the fact that it is identical with the thermodynamic scale and is closely approached in some regions by actual gases.

The upper limit to which the gas thermometer can be used in establishing the thermodynamic, or absolute, scale of temperature is set by the properties of the container for the gas. No suitable container has been found to allow one to go above 1500°C. Actually, the readings of a gas thermometer are not accepted for establishment of the absolute scale above the gold point (1063°C.). There are, of course, many instances where one desires to measure temperatures higher than this. Various properties might be used at these elevated temperatures, such as the expansion of some solid or the thermoelectric power of dissimilar metals, but there is again the question of establishing the absolute scale. This is done with the aid of the laws of radiation, which have been well established at temperatures below 1500°C. and may be extrapolated with reasonable confidence.

The lower limit of temperature is set by that of the absolute zero, which is definitely known to be close to 273.2°C. below the ice point, and in recent research work it has been possible to produce and measure temperatures that are only a few hundredths of a degree above the absolute zero. There is presumably no upper limit. Astronomers speak of stars with temperatures of millions of degrees, but this involves a very great extrapolation of known facts. The highest terrestrial temperatures are those in arcs that have been variously estimated as lying between the limits of 3800 and 10,000°C. abs.

The International Scale.[1]—This is a scale agreed upon by various standardizing laboratories of the world as the best approximation to the thermodynamic scale for practical purposes. It is based on the fol-

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[1] BURGESS, G. K., *Bur. Standards J. Research*, **1**, 635 (1928).

lowing fixed points (points of phase change) at a pressure of 1 standard atmosphere:

°C.

Boiling point of oxygen...................	−182.97
Ice point...............................	0.000
Boiling point of water...................	100.000
Boiling point of sulphur.................	444.60
Freezing point of silver.................	960.5
Freezing point of gold...................	1063

} by definition (for Ice point and Boiling point of water)

Interpolation is by means of the platinum-resistance thermometer from −190 to 660°C. and the platinum, platinum-rhodium thermocouple from 660 to 1063°C., suitable interpolation formulas being agreed upon. Above the gold point, the international scale is defined by an optical pyrometer the readings of which are related to temperature by the equation

$$\ln \frac{J_2}{J_1} = \frac{C_2}{\lambda}\left(\frac{1}{1336} - \frac{1}{t_2 + 273}\right) \tag{I.2}$$

where J_2 = intensity of monochromatic visible radiation emitted by a black body at the unknown temperature t_2.

J_1 = intensity of radiation of same wave length from a black body at the gold point.

λ = wave length, cm.

C_2 = an empirical constant.   In centimeter-degrees $C_2 = 1.432$.

For use in calibrating temperature-measuring instruments, the secondary fixed points in Table I.2 are available.

TABLE I.2.—SECONDARY FIXED POINTS FOR CALIBRATION OF TEMPERATURE MEASURING DEVICES*

Substance	Value, °C., on the International Temperature Scale
Sublimation point of carbon dioxide.......................	−78.5
Freezing point of mercury...............................	−38.87
$Na_2SO_4 \cdot 10H_2O$ transition point...........................	32.38
Boiling point of naphthalene............................	217.96
Freezing point of tin...................................	231.9
Boiling point of benzophenone........	305.9
Freezing point of cadmium..............................	320.9
Freezing point of lead..................................	327.3
Freezing point of zinc..................................	419.4
Freezing point of antimony.............................	630.5
Freezing point of aluminum.............................	660.1
Freezing point of Cu-Ag eutectic........................	778.8
Freezing point of copper................................	1083.0
Melting point of palladium.............................	1555
Melting point of platinum..............................	1773
Melting point of tungsten..............................	3400

* Burgess, G. K., *Bur. Standards J. Research*, **1**, 635 (1928).   Roeser, W. F., and H. T. Wensel, *ibid.*, **14**, 247–282 (1935).

There is no internationally accepted temperature scale below 90°K. Temperatures between 90 and 14°K. may be measured by platinum-resistance thermometers for which the Bureau of Standards has recently[1] established a scale by comparison with the helium-gas thermometer. Two fixed points are available in this range, *viz.*, the boiling point of hydrogen (20.39°K.) and the triple point of hydrogen (13.96°K.). Temperatures between 14°K. and absolute zero require special methods, a discussion of which is beyond the scope of this book.

PRESSURE

The second most important variable in any thermodynamic discussion is pressure. It involves a considerably simpler concept than temperature in that it can be directly related to the fundamental units of mass, length, and time.

Pressure is defined as force per unit of area. In the absolute system of units, pressure may be expressed in dynes per square centimeter or in poundals per square foot, depending on whether metric or English units are used; in the gravitational system, in grams per square centimeter or pounds per square foot. 1 g. per sq. cm. = g dynes per square centimeter, where g is the acceleration of gravity in centimeters per second per second. In engineering work, gravitational units are used almost exclusively, and the commonest unit of pressure is pounds per square inch.

Pressures are frequently measured in terms of the height of a column of fluid that the pressure will balance. The relation between the head h of the fluid above a given plane and the pressure p in gravitational units at that plane is given by the simple equation $p = h\rho$ where ρ is the density of the fluid. With h in feet and ρ in pounds per cubic foot, p will be in pounds per square foot. In very accurate work, since ρ varies with the temperature, h should be referred to some temperature. Furthermore, to convert to absolute units, which is necessary if accurate measurements are to be compared between different laboratories, the latitude and elevation above sea level should be given.

Another commonly used unit of pressure is the atmosphere, which, as its name implies, is the pressure caused by the weight of the earth's atmosphere. Since this is not a constant, the unit has to be defined more specifically. A standard atmosphere is defined as the pressure due to a vertical column 760 mm. long of pure mercury having a density of 13.5951 g. per cc. (density at 0°C.) and in a location at sea level at 45° latitude where $g = 980.665$ cm. per sec.[2] Pressure is also expressed in bars, also known as "metric atmospheres." 1 b∙r = 10^6 dynes per square centimeter = 0.9869 atm.

[1] Hoge, H. J., and F. G. Brickwedde, *Bur. Standards J. Research*, **22**, 351 (1939).

In engineering work, pressures are commonly measured above a datum established by the prevailing atmospheric pressure, and such pressures are known as "gauge pressures." Absolute pressure is the sum of the pressure as read by a gauge open to the atmosphere and the barometric pressure at that point. A space from which all gas has been removed would be a perfect vacuum and at zero pressure. The best vacuum pumps will enable one to reach vacuums as low as 10^{-9} mm. This seems like a very small pressure, but actually it is very far from being empty space, for a gas at this pressure and at 0°C. would still have 2×10^8 molecules for every cubic centimeter. The nearest approach to an absolute vacuum is interstellar space, where the density is estimated to be of the order of 10^{-30} g. per cc. or about one molecule of H_2 for every 100 cu. ft.

Pressures below atmospheric, or vacuums, are commonly expressed in millimeters or inches of mercury gauge. This leads to a good deal of confusion, for a 28-in. vacuum means one thing when the barometer is 28.01 in. and quite another thing when the barometer is 30.5 in. The first would be a high vacuum unattainable with the ordinary mechanical pumps, whereas the second one would be quite easy to reach. Gauge pressures are satisfactory if referred to a definite barometer; but frequently the reference barometer is not given, and it would be better for this reason to use absolute pressure.

Pressures up to 135 atm. (2,000 lb. per sq. in.) are relatively common in engineering practice. Pressures up to about 1,000 atm. (15,000 lb. per sq. in.) are used industrially. Pressures of the order of 50,000 lb. per sq. in. are common in heavy artillery, and pressures as high as 3,000,-000 lb. per sq. in. have been produced in certain experimental work in laboratories.

DEFINITION OF STATE

In this chapter we are attempting to define a number of general terms and concepts that are in common use but that are difficult to define in any rigorous manner. Let us recognize at the start that the definitions are only general guides and that there are always special cases to which the stated definitions do not strictly apply and for which some modifications are in order.

Macroscopic vs. Microscopic State.—In giving the properties of any substance or mixture of substances it is absolutely essential to note the state in which the given system exists. We shall have frequent occasion to refer to substances in various states, and it is desirable at the outset to consider very briefly just what is meant by the state of a substance in the thermodynamic sense.

If we confine a sample of gas at a fixed temperature and pressure, its other properties such as density, viscosity, refractive index, and thermal conductivity are definitely determined. We have defined its state in a

gross sense. Any sample of the same pure gas brought to the same temperature and pressure will exhibit identical properties. But the gas consists of an aggregate of a very large number of individual particles or molecules in rapid motion. If we wished to deal with the individual particles, it would be necessary to define the position, the velocity, and the direction of motion of each one. This is the method of approach used in a kinetic treatment, and the kind of state defined is conveniently called a "microscopic" state. Obviously, a very large number of variables is needed to treat systems in this way, and the mathematical methods used in arriving at measurable quantities by means of deductive reasoning are generally classified under the general head of statistical mechanics.

On the other hand, the kind of state we mean in any thermodynamic treatment is a "macroscopic" state, or one that is a statistical average of the microscopic states. We employ certain gross variables, the resultants of the actions of the microscopic variables. Thus our concepts of pressure and temperature are simply such statistical quantities. This point of view is important because it is the very essence of the whole thermodynamic method of approach to a problem. Using a crude analogy, we cannot predict what individuals will do in a given situation, but we can usually predict with considerable accuracy what a crowd or large group of individuals will do. This is a matter of probability; thus we see that thermodynamics is closely linked with chance and probability.

It is also important to note that this method of treatment does not require any assumptions in regard to the structure of the mediums with which it deals. It treats them as if they were continuous rather than being composed of discrete particles as we know them to be.

Systems, Components, and Variables.—We shall now proceed to define certain general terms and concepts that will be used very frequently. A system will refer to any specified part of the material universe that we choose to set apart for study. The rest of the universe, and more particularly that immediately adjacent to the system, will be known in general as the "surroundings." A homogeneous system is one in which the properties in a gross, or macroscopic, sense either are the same from point to point or change in a continuous manner. There are no regions where there are discontinuities or abrupt changes. Such a homogeneous system is called a "phase." A heterogeneous system is one that consists of more than one phase, and at the phase boundaries there will be sudden or abrupt changes in properties. Systems consisting of only gases or vapors are always homogeneous. No one has ever observed more than one gas phase. With liquids, two phases are common; in the case of solids, any number of different phases are possible within limits set by other conditions.

A solution is a homogeneous (*i.e.*, single-phase) system consisting of more than one component. Solutions in which the individual particles are of molecular dimensions are often referred to as "true" solutions to distinguish them from colloidal solutions, where the individual particles of at least one of the components are large aggregates and approach the condition of separate phases. There are many borderline cases here, and no sharp distinction can be drawn; but our use of the term "solution" will refer to true solutions.

The term "component" has a special meaning in all thermodynamic arguments; it will be necessary to consider several examples in order to obtain a clear conception of its meaning. Consider such a simple system as pure water, H_2O. We recognize the existence of several different chemical species or constituents that may be formed from the single chemical substance H_2O. We might have the following reactions occurring:

$$H_2O = H^+ + OH^-$$
$$2H_2O = (H_2O)_2$$
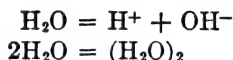
Thus we may have four different chemical constituents present, *viz.*, H^+ ions, OH^- ions, H_2O molecules, and $(H_2O)_2$ molecules, but there is only *one component* in the system. All the constituents are instantly derivable from a single species H_2O and are not *independently variable*.

Ordinary water contains a small amount of deuterium oxide, a chemical individual very similar in its properties to H_2O but containing the heavy hydrogen isotope. This species is not instantly derivable from H_2O, and hence ordinary water is not strictly a single-component system; but as long as the D_2O is present in a very small concentration that is constant, ordinary water can be treated as a single component for most practical purposes. If, however, one were to study the properties of special water produced by adding varying amounts of D_2O to ordinary water, then the system must, of course, be regarded as having two components.

One of the confusing things about the definition of number of components is the way the number may change with circumstances even though the system always contains the same chemical species. For example, a system containing H_2O, H_2, and O_2 may be either two or three component, depending on the circumstances. If we are studying the solubility of a mixture of hydrogen and oxygen of varying proportions in water, the system is three-component since each one of the chemical individuals is independently variable and the state of the system can be defined only by specifying the proportion of each that is present.

If, on the other hand, we are studying the chemical equilibrium between water vapor, hydrogen, and oxygen at high temperatures, then

the system with the same three chemical species is only two-component. This follows from the fact that any composition of the equilibrium mixture can be produced from any two of the chemical individuals. There is an additional restraint on the system, and it is no longer possible to vary all three substances at will.

Now consider a system consisting of an aqueous solution in which the following ions are present: K^+, Na^+, Cl^-, and Br^-. Such a system might be produced by dissolving KCl, NaCl, KBr, and NaBr in water, and it might appear at first sight that this was a five-component system. This is not the case, however, because some of the constituents could have been produced from others by the reaction

$$NaCl + KBr = NaBr + KCl$$

For example, the system might have been produced from H_2O, NaCl, and KBr and hence be three component. This would result, however, in a fixed ratio of NaBr to KCl, and if we wish to have complete freedom in making any desired composition we must start with three salts. We conclude, therefore, that the complete system can be produced by independent variation of any four of the constituents and so is a four-component system.

Another way to consider this question is the following: Ordinary methods of chemical analysis would reveal the presence in the solution of the constituents H_2O, H^+, OH^-, K^+, Na^+, Cl^-, and Br^-. The H^+ and OH^- could have come only from H_2O and so are not independently variable. K^+, Na^+, Cl^-, and Br^- are not all independently variable because there is the necessary condition that the solution must be electrically neutral and imposing this condition of restraint on the four constituents leaves three independently variable.

We may sum up by formally defining the number of components as the least number of independently variable chemical substances from which the given system in all its variations could be produced.

A property is something definitely associated with the state of a substance. Once the state is fixed the properties are all fixed (but not necessarily known). The variables commonly chosen to represent the state are pressure, volume, temperature, and the masses of the components in each phase. Not all these variables are independent. In the case of a pure gas, if one fixes the volume, mass, and temperature, then the pressure is fixed. It is a dependent variable and depends on the state fixed by the volume and temperature just like any property. The number of independent variables or the number of variables whose value must be stated before the state is definitely fixed is called the "degrees of freedom." The system of a pure gas just discussed has two degrees of freedom, or it may be said to be a "bivariant" system. On the other

hand, water in phase equilibrium with its vapor has only one degree of freedom, or is a "univariant" system. When either the temperature or the pressure is fixed, the state and hence the properties are fixed. If we try to fix arbitrarily both the temperature and the pressure, then we shall find that one of the phases will disappear in the process so that the system becomes bivariant. A system in which three phases of the single component, water, coexist would be a nonvariant system, *i.e.*, one having no degrees of freedom. Both the pressure and the temperature would be fixed, and neither could be varied without causing the disappearance of a phase. That extraordinarily useful and important relationship between the number of components, phases, and degrees of freedom of any system, known as the "phase rule," will be derived in a later chapter.

Composition of a Solution.—This may be stated merely by giving the mass of each constituent present, such as N_A moles of A or N_B moles of B. It is more convenient, however, to express composition in terms of ratios of masses. For example, in a solution containing m_A lb. of A, m_B of B, etc., the composition could be represented in terms of weight fractions (or weight per cent) thus:

$$r_A = \frac{m_A}{m_A + m_B + m_C + \cdots} \tag{I.3}$$

where r_A = weight fraction of A.

A similar equation expresses the mole fraction x_A in terms of the number of moles of A and the total. In certain cases, notably in the unit operation of absorption, it is convenient to express the composition of a binary solution by means of the ratio of the mass of one component to that of the other.

In a system of N components there will be only $(N - 1)$ independent composition variables because of the following relationship between them:

$$x_A + x_B + x_C + \cdots + x_N = 1 \tag{I.4}$$

Composition is sometimes expressed as volume fraction. If there is a volume change on mixing, this is apt to cause considerable confusion, for per cent by volume can be interpreted in different ways, and the various percentages of all the components will not add up to 100 per cent. In the case of gases, the volume fraction is generally taken to mean the volume decrease resulting from the removal of a given constituent, divided by the original volume. Since gases form substantially ideal solutions, *i.e.*, no volume changes occur on mixing, there is no ambiguity. Now consider the case where 50 cc. of liquid A is added to 50 cc. of liquid B, resulting in 95 cc. of mixture. This mixture might be said to contain either 50 per cent A or 52.5 per cent A, depending on the

definition of per cent by volume. If we give the per cent of A as 52.5 per cent, then the per cent of B is not 47.5 per cent but also 52.5 per cent. It is better to avoid the use of per cent by volume except for the case of gases.

FUNDAMENTAL EQUATIONS RELATING PROPERTIES AND VARIABLES

If G represents any property of a system, whose state is defined by the three independent variables p, t, and x, then we may write,

$$G = \phi(p,t,x)$$

This simply means that the value of G is definitely fixed whenever the values of p, t, and x are fixed. The way in which G changes as we change the values of these variables is given by the well-known equation of the differential calculus,

$$dG = \left(\frac{\partial G}{\partial p}\right)_{t,x} dp + \left(\frac{\partial G}{\partial t}\right)_{p,x} dt + \left(\frac{\partial G}{\partial x}\right)_{p,t} dx \tag{I.5}$$

The change in G can be regarded as the net result of three independent changes, the first one due to p alone, t and x being constant, the second due to t alone, p and x being constant, and the third due to x alone. For the sake of simplicity in the discussion to follow, x will be regarded as constant, reducing the independent variables to p and t.

Change of Independent Variable.—It often happens that we have a change in a property expressed as a function of one set of independent variables and we wish to change to another set. Thus, suppose we have

$$G = \phi_1(p,t) \tag{I.6}$$

and also let
$$p = \phi_2(v,t) \tag{I.7}$$

where the pressure is now a dependent variable. Now suppose that we wish to express G in terms of v and t as the independent variables, with p becoming a dependent variable. From Eq. (I.6) we have

$$dG = \left(\frac{\partial G}{\partial p}\right)_t dp + \left(\frac{\partial G}{\partial t}\right)_p dt \tag{I.8}$$

Now, since
$$p = \phi_2(v,t)$$

we can write
$$dp = \left(\frac{\partial p}{\partial v}\right)_t dv + \left(\frac{\partial p}{\partial t}\right)_v dt \tag{I.9}$$

Substituting the value of dp from Eq. (I.9) into Eq. (I.8),

$$dG = \left(\frac{\partial G}{\partial p}\right)_t \left[\left(\frac{\partial p}{\partial v}\right)_t dv + \left(\frac{\partial p}{\partial t}\right)_v dt\right] + \left(\frac{\partial G}{\partial t}\right)_p dt$$

$$= \left(\frac{\partial G}{\partial p}\right)_t \left(\frac{\partial p}{\partial v}\right)_t dv + \left[\left(\frac{\partial G}{\partial p}\right)_t \left(\frac{\partial p}{\partial t}\right)_v + \left(\frac{\partial G}{\partial t}\right)_p\right] dt \tag{I.10}$$

Also,
$$dG = \left(\frac{\partial G}{\partial v}\right)_t dv + \left(\frac{\partial G}{\partial t}\right)_v dt \tag{I.11}$$

Now since the change in G has only one value for a given change in v and t, the coefficients of dv and dt in Eqs. (I.10) and (I.11) must be equal. Therefore,

$$\left(\frac{\partial G}{\partial v}\right)_t = \left(\frac{\partial G}{\partial p}\right)_t \left(\frac{\partial p}{\partial v}\right)_t \tag{I.12}$$

and

$$\left(\frac{\partial G}{\partial t}\right)_v = \left(\frac{\partial G}{\partial t}\right)_p + \left(\frac{\partial G}{\partial p}\right)_t \left(\frac{\partial p}{\partial t}\right)_v \tag{I.13}$$

Other related equations can be obtained from Eqs. (I.12) and (I.13) merely by interchanging subscripts. Thus, interchanging p and t in Eq. (I.12),

$$\left(\frac{\partial G}{\partial v}\right)_p = \left(\frac{\partial G}{\partial t}\right)_p \left(\frac{\partial t}{\partial v}\right)_p \tag{I.14}$$

Change at Constant G.—Suppose that we are interested in a change during which the property G remains constant. In such a case $dG = 0$ and we can write Eq. (I.8) in the form

$$\left(\frac{\partial G}{\partial p}\right)_t dp_G + \left(\frac{\partial G}{\partial t}\right)_p dt_G = 0 \tag{I.15}$$

The subscript G on dp and dt indicates that these two changes are at constant G. (In general, in writing equations containing partial derivatives we shall give the subscript only in those cases where it is not obvious what was constant during the differentiation.) Equation (I.15) may also be put in the following form:

$$\left(\frac{\partial p}{\partial t}\right)_G = -\frac{(\partial G/\partial t)_p}{(\partial G/\partial p)_t} \tag{I.16}$$

The following equation, useful in certain cases, may be derived by similar methods:

$$\left(\frac{\partial p}{\partial t}\right)_G \left(\frac{\partial t}{\partial v}\right)_G = \left(\frac{\partial p}{\partial v}\right)_G \tag{I.17}$$

For the special case where $G = v$, Eq. (I.16) can be put in the following useful form:

$$\left(\frac{\partial p}{\partial t}\right)_v \left(\frac{\partial v}{\partial p}\right)_t \left(\frac{\partial t}{\partial v}\right)_p = -1 \tag{I.18}$$

Equality of the Second Derivatives.—Since the value of a property depends on the particular state, it should be clear that the change in the value of a property when the system changes from state 1 to state 2 is a constant amount independent of how the change was brought about—in other words, independent of the particular path or the particular

mechanism used. This exceedingly simple and almost obvious statement presents a principle of far-reaching importance and one whose application may very easily be unrecognized in many actual cases. For purposes of derivation it is conveniently expressed by the following equation for the case of two independent variables:

$$\frac{\partial^2 G}{\partial p\,\partial t} = \frac{\partial^2 G}{\partial t\,\partial p} \qquad (I.19)$$

This equation merely says that the value of the second derivative is independent of the order in which the two differentiations are performed. Its meaning may be further clarified by giving a simple derivation of it. Referring to Fig. I.1, consider the change in G in going from A to B along any path such as AB. For the sake of simplicity consider only an infinitesimal change so that $G_B - G_A = dG$. Since the change must be independent of the path followed, consider it to take place along the path ADB. As the change from A to D is one at constant pressure, we may write

Fig. I.1.—Illustrating derivation of Eq. (I.19).

$$G_D = G_A + \left(\frac{\partial G_A}{\partial t}\right)_p dt \qquad (I.20)$$

Similarly, for the constant-temperature path DB,

$$G_B = G_D + \left(\frac{\partial G_D}{\partial p}\right)_t dp \qquad (I.21)$$

Differentiating G_D with respect to pressure and substituting in Eq. (I.21),

$$G_B = G_A + \left(\frac{\partial G_A}{\partial t}\right)_p dt + \left(\frac{\partial G_A}{\partial p}\right)_t dp + \frac{\partial^2 G_A}{\partial t\,\partial p}\,dp\,dt \qquad (I.22)$$

In an exactly analogous manner, for the path ACB, we obtain

$$G_B = G_A + \left(\frac{\partial G_A}{\partial p}\right)_t dp + \left(\frac{\partial G_A}{\partial t}\right)_p dt + \frac{\partial^2 G_A}{\partial p\,\partial t}\,dt\,dp \qquad (I.23)$$

Since $G_B - G_A$ must be the same for the two paths, it is necessary that Eq. (I.19) be true, as may be seen by equating Eqs. (I.22) and (I.23).

Integral Changes.—In a practical case one is more interested in a finite change of G from state A to state B. To consider again only two independent variables, the integral form of Eq. (I.8) is

$$G_B - G_A = \int_{p_1}^{p_2}\left(\frac{\partial G}{\partial p}\right)_t dp + \int_{t_1}^{t_2}\left(\frac{\partial G}{\partial t}\right)_p dt \qquad (I.24)$$
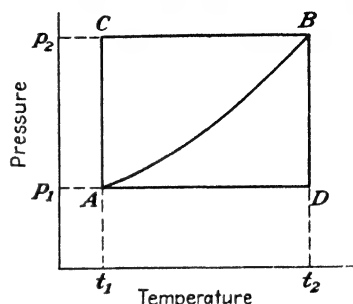
In order to make the illustration more concrete, let us consider an actual thermodynamic property such as H, enthalpy. For a pure substance, it will be shown later that the following equations hold:

$$\left(\frac{\partial H}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$$

and

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

Substituting in an equation of the form of Eq. (I.24),

$$H_2 - H_1 = \int_{p_1}^{p_2}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp + \int_{T_1}^{T_2} C_p\,dT \qquad (I.25)$$

The integrations may be performed either graphically or analytically, depending on circumstances. It is important to note that the integration can be performed in two different ways requiring somewhat different sets of data. Thus we may integrate first at the constant temperature T_1 and evaluate the first integral. To do this we must know how v and the slope of the vT curve at constant pressure change with the pressure at the *one temperature* T_1 over the range of pressure from p_1 to p_2. H_1 is the value of H at the starting point p_1, T_1 and must be known from other considerations. The result of the first integration will be the value of H at p_2 and T_1. The second integration is then performed at the constant pressure of p_2, and the data needed would be the variation of C_p with the temperature at the *constant pressure p_2*.

The integration can equally well start with the constant-pressure integral, in which case the data required are C_p as a function of T but now at the constant *initial pressure p_1*. The second, or constant-temperature, integration is now carried out at T_2 instead of T_1. These two ways are illustrated by Fig. I.1. The first way corresponds to following the path ACB, and the second follows path ADB. It should be clear from the nature of a property that both lead to the same result and that the choice is a matter of convenience, depending on the data available.

REPRODUCIBILITY OF STATES

The previous paragraphs have implied that, if we fix all the independent variables, the state (macroscopic) of any system is definitely fixed. In other words, if any substance of given composition is subjected to a complex series of changes and then the independent variables are fixed at their initial values, the substance will have properties in the final state identical with those in the initial state. Another way of stating this is that the properties depend only on the variables of state *and not on the previous history*. This is rigorously true in the case of gases and in most cases for liquids but may be far from true in the case of solids. As long

as the molecules can move around freely as in a gas or liquid, they will instantly arrive at an equilibrium state (not a static equilibrium but a dynamic one representing a statistical equilibrium) and the properties will not change with time. In the case of solids where this complete freedom of motion does not exist, changes in the structure will occur which are not reversed when the initial set of external variables is established and the solid does not have the same properties that it originally had under these identical conditions. Presumably, slow changes are occurring, and if sufficient time were allowed it would reach an equilibrium state in which the properties were fixed and reproducible. The stable state for a solid is the crystalline state, which means a completely ordered arrangement, and the ideal would be the solid in the form of a single crystal.

A few concrete examples will illustrate these ideas. The properties of metals can be profoundly modified by heat-treatment or by cold-working; thus, a material of given composition at a given pressure and temperature may exhibit quite different properties according to its previous history. Carbon may be obtained in various forms, two differing considerably in properties being carbon black and graphite. A metal such as copper can be obtained in the form of massive crystals by slowly cooling molten copper or in wholly different form by reducing copper oxide at a relatively low temperature. These two forms of copper would look quite different and would have some strikingly different properties. The one would be pyrophoric and would be active in promoting certain chemical reactions (catalytic effect) whereas the other would be entirely inert in these respects. The difference is not primarily one of mechanical subdivision because an impalpable copper powder produced by atomizing molten copper would still be quite different from that produced by low-temperature reduction of the oxide.

Of course, the question of surface is an important factor in these effects. Thus it is well known that a salt in the form of very minute crystals is slightly more soluble in a liquid than the same substance in the form of coarse crystals. This is a manifestation of surface energy, and it is a well-known fact that any system with extended surface tends to change in such a way as to reduce the surface energy. On the other hand, mere extent of surface is not the whole story. The work on heterogeneous catalysis has amply demonstrated that there are important qualitative differences in surfaces which cause them to exhibit quite different properties even when the areas are approximately the same.

The question of the reproducibility of the state of a solid is also complicated by the fact that some solids are exceedingly difficult to obtain in a pure state and that even traces of impurities may greatly modify the propertres. To take the case of metals again, very small amounts of

impurities, especially nonmetals such as oxygen, sulphur, and phosphorus, profoundly affect the properties. Many of the properties we commonly associate with a given metal are frequently due mainly to an impurity. When we produce carbon by thermal decomposition of a hydrocarbon, or a metal oxide by precipitation from solution, the question of composition as well as structure enters.

All this means that when we deal with the thermodynamics of changes involving solids we must realize these facts and attempt either to bring all solids to the equilibrium, crystalline state or at least to recognize that there will be these differences of properties. If we speak of the heat of combustion of carbon, we should be careful to state what form of carbon is meant. When we make up an electrochemical cell involving certain solids in the reaction and have solids for electrodes, we must realize that the e.m.f. will vary with the previous history of the solids involved unless they are brought to their equilibrium states. When we deal with solids in this book, it will be implied, unless otherwise stated, that the solid is supposed to be in its most stable state or at least close enough to it so that the difference in thermodynamic properties is negligible.

STANDARD STATES

Since we shall deal very largely with properties that have no known absolute values and therefore shall be concerned with differences of the property between two states, when we give numerical values of properties of substances and systems, it will be convenient to regard certain states of a substance as reference, or standard, states. The choice of a standard state is purely arbitrary and may vary, depending on the application in question. In many cases, the standard state refers only to an initial state of pressure or concentration along an isotherm and has no reference to any particular temperature. In other cases, a certain temperature is also selected. Thus, in giving values of certain thermodynamic functions such as enthalpy or entropy, the value of the function is considered to be zero at a reference state of 0°C. and 1 atm. absolute pressure when the substance is in a state of aggregation that is the commonest one at room temperature, though one may, in special instances, prefer to use other reference states. Thus, for CO_2 the reference state would commonly be the gas at 0°C. and 1 atm., and for H_2O it would be liquid water.

In giving data on heats of chemical reaction or free energies of reaction and other changes in properties of a similar nature, the usual reference temperature is 25°C. (298.2°K. or C. abs.), and each substance is assumed to be in its most stable form, in a pure state at 1 atm. pressure.

Thus for the reaction

$$CO + H_2O\,(l) = CO_2 + H_2$$
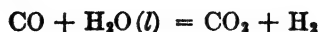
let ΔG be the change in property desired at 25°C.

$$\Delta G = G_{H_2} + G_{CO_2} - G_{CO} - G_{H_2O}$$

where each value of G is for the respective substance in the pure state at 25°C. and 1 atm. pressure. Since we are dealing with properties, the actual path by which the reaction takes place is entirely immaterial. It is necessary to specify definite initial and final states only.

In the illustration chosen the water was in the liquid state, which is the stable state for the given conditions. It is common practice to give values for the same reaction involving gaseous water. Since water does not exist in stable equilibrium as a gas at this temperature and pressure, this means that the standard state chosen is a hypothetical one. To evaluate the property we must make an extrapolation from the known value in a stable state (25°C. and the vapor pressure at this temperature, for example) to the hypothetical state. This is incorrect in principle but is frequently justified on the grounds of convenience; and, with a slight extrapolation, the error cannot be great.

In the case of liquids and solids it is generally not important always to state the standard pressure, for the properties change very little with pressure. In the case of gases it may be important. A commonly chosen reference, or standard, state for a gas at any given temperature is a pressure, $p°$, low enough so that the gas can be considered ideal. For practical purposes this can usually be regarded as 1 atm. abs.

In dealing with solutions, the standard state for any component may be chosen as the pure substance at the same temperature and 1 atm. pressure, or it is sometimes more convenient to choose as the standard state a purely fictitious one, as we shall see later (page 121). Reasons for this difference can best be made clear when an actual case arises.

WORK AND POWER

Definition of Work.—Work is done whenever a system acts against an external force. It is expressed as the product of an intensity factor and a capacity, or amplitude, factor. For ordinary mechanical work the intensity factor is force and the capacity factor is the distance through which the force acts. Therefore W (work) $= F$ (force) $\times L$ (distance); or if the force is a variable one, we should write $W = \int_{L_1}^{L_2} F \, dL$, which can be evaluated if F can be expressed as a function of L.

In addition to mechanical work, which involves the action of mechanical forces, we may have other kinds of work, depending on the nature of the force acting. Work may be done by the action of an electrical force or, more strictly, an e.m.f., represented by E. In this case the capacity, or amplitude, factor is Q, the quantity, or charge, of electricity,

usually expressed in coulombs. Hence, electrical work $= \int_{Q_1}^{Q_2} E \, dQ$. Analogous expressions for work are

$$\text{Surface-tension work} = \int_{S_1}^{S_2} \sigma \, dS$$

where σ = surface tension and S = surface area.

$$\text{Work against the force of gravity} = \int_{z_1}^{z_2} mg \, dz$$

where m = mass.

g = acceleration of gravity.

z = height in a gravitational field above some designated datum level.

In the thermodynamic sense, work is concerned only with action against forces *external* to the system. There is no such thing as "internal" work, and it only adds to the confusion to use this term. One illustration may help to clarify this. Suppose a gas confined at high pressure in one cylinder expands through a valve into another closed cylinder at lower pressure (Joule experiment). If the system is the gas in *both* cylinders, no work is done. If, on the other hand, the system under consideration is just the gas in the first cylinder up to the throttle valve, this gas does work on external forces.

Work Due to Fluid Pressure.—The case of work done by or against a fluid pressure is an especially important case for the mechanical engineer and chemical engineer. Since pressure is force per unit area A, the general expression for mechanical work may be written

$$dW = pA \, dL$$

but $A \, dL$ is a change in volume, and so

$$dW = p \, dV$$

or
$$W = \int_{V_1}^{V_2} p \, dV \qquad (1.26)[1]$$

If the pressure is constant, this reduces to

$$W = p(V_2 - V_1)$$

or $p \, \Delta V$. When the pressure is not constant, its change with volume must be known in order that the expression for the work can be integrated. If the pV relationship can be expressed by a simple formula, the integration could conveniently be performed algebraically. If the relationship is known but not amenable to simple formulation, the integration may be performed quite simply by graphical means. From the

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[1] It is to be noted that, in all calculations of work against a fluid pressure, the pressure should be *absolute* and not *gauge* pressure.

calculus it is well known that the value of the integral is the area under the curve of p vs. V down to the $p = 0$ axis between the given volume limits. For example, it is the shaded area in Fig. I.2, where curve AB represents the relationship between p and V. The area may be obtained by planimeter or very simply by counting squares on cross-section paper.

Indicator Diagram.—In the case of a continuously operating engine such as a gas compressor or a steam engine, the fluid goes through a cycle of changes, returning to the starting point. Figure I.3 represents a somewhat idealized cycle on the pV diagram, consisting of four different changes occurring during the course of two strokes of a piston.[1] As in the previous case the work for each change is the area under each pV line to the $p = 0$ axis, and the total work is the algebraic sum of the four individual items. Two of the changes are with the piston moving from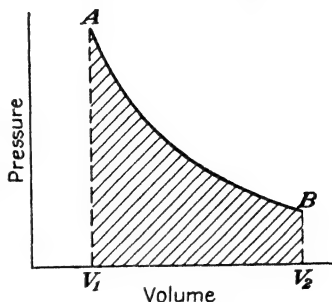 right to left and represent (in the case of a compressor) work done on the gas by the piston, whereas, in the other two, the piston is moving in the opposite direction and work is done by the gas on the piston. Therefore, two of the work terms must be represented as opposite in sign to the others in the algebraic summation. From the geometry of the figure, it can readily be seen that the summation of the individual areas equals the enclosed (crosshatched) area.

FIG. I.2.—Work from the area under a pV curve.

(Area $DCC'D' +$ area $ADD'A' -$ area $ABB'A' -$ area
$$BCC'B' = \text{area } ABCD.)$$

This leads to the generalization that, for any cycle represented on the pV diagram, the work is equal to the enclosed area. By means of a device known as an "indicator," engines can be made to trace automatically the cycle of pV changes occurring in a cylinder, and from this "indicator diagram" the work can at once be obtained. Work obtained in this way is frequently denoted "indicated work." It will be the work per cycle and, when multiplied by the number of cycles in a given time, will be the work done over that period of time. A cycle such as that illustrated in Fig. I.3 can be of two kinds, a closed cycle or one representing a flow process. In the former, the mass is the same in all parts of the cycle, and change in volume represents a change in state of the fluid. In the flow process, a charge is drawn into a cylinder along the path AB, and

[1] It should be noted, however, that the amount of fluid is not the same in all parts of the cycle and that a fresh charge is drawn in once during each cycle. In other words, we are not considering a *closed* cycle.

the volume change is due to an increase in mass and does not represent a change of state. The work along such a path will be known as "injection work." Similarly, the path CD represents a discharge of material from the cylinder, and the work along it will be called "ejection work." Paths BC and DA represent changes of state at constant mass just as in the case of the closed cycle. The expression for the net work of the cycle will be the same for the two cases provided that one always uses the *total* volume.

Power.—Power is the time rate of doing work, or, mathematically,

$$P = \frac{dW}{d\theta} \tag{I.27}$$

For the case of electrical work, this becomes,

$$P = \frac{E\,dQ}{d\theta} = EI$$

since the current I is, by definition, equal to $dQ/d\theta$.

Fig. I.3.—Work for a cycle on the pV diagram.

For mechanical work against a fluid pressure,

$$P = p\,\frac{dV}{d\theta} \tag{I.28}$$

It can readily be seen that the doing of a relatively small amount of work may nevertheless involve a large amount of power if the time interval is very short. Familiar examples are a blast of high explosives or a lightning stroke.

In some cases one is concerned with the determination of the total work done over a period of time when power is being expended at a known rate. From Eq. (I.27) we can get

$$W = \int_{\theta_1}^{\theta_1} P\,d\theta \tag{I.29}$$

and W can be obtained from a knowledge of the variation of the power with time.

Certain instruments such as a wattmeter measure power directly and the determination of total energy expended in work could be made by means of Eq. (I.29), given a power-time curve. A watt-hour meter performs this integration automatically.

If the power is expended at a uniform rate, then

$$W = P\,\Delta\theta \qquad \text{or} \qquad P = \frac{W}{\Delta\theta}$$

Thus the uniform expenditure of power to compress 1,000 cu. ft. of air per hour under given conditions would be the work to compress this volume divided by the time interval.

Units of Work and Power.—Mechanical work is expressed in foot-pounds (distance times force), cubic foot–atmospheres (pV product), liter-atmospheres, and similar units, none of which has been named. Mechanical power would be expressed in units of work divided by time, or foot-pounds per minute, liter-atmospheres per hour, etc. A horsepower is arbitrarily defined as 33,000 ft.-lb. per min. (or 550 ft.-lb. per sec.). Since power × time = work, work is frequently expressed in power-time units such as horsepower-hours. Electrical work would be expressed in volt-coulombs (also called "joules") or volt-equivalents (an equivalent is based on the Faraday laws of electrochemistry and is equal to the number of coulombs associated with 1 gram equivalent of an ion) and power in volt-coulombs per second or volt-amperes, usually called "watts." Analogous to mechanical work, electrical work may also be expressed in watt-hours and other similar units. In Table II in the Appendix there are given conversion factors for various units of energy.[1] Power equivalents will be the same except for the different time factors that may be involved.

HEAT

Prior to the beginning of the nineteenth century, heat had been regarded as an imponderable material fluid, known as "caloric." The qualitative experiments of Count Rumford toward the close of the eighteenth century on the development of heat by friction with a blunt boring tool and the experiments of Davy in which ice was melted purely by the mechanical process of rubbing, dealt a deathblow to this idea and established heat as a form of energy due to the motion of the individual molecules of which matter is composed. It was not until Joule performed his famous quantitative experiments on the relationship between heat and other forms of energy, about the middle of the century, that the older idea was completely rejected and heat was firmly established as a form of energy.

Thermodynamic Definition.—In thermodynamics the term "heat" is strictly used in a somewhat narrower sense, and it is important for a

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[1] "Energy" is commonly used as a general term embracing both heat and work and also to refer to a capacity, resident in a system, for doing work or for transferring heat. A more exact definition of the thermodynamic property called "energy" or "internal energy" will be given in the next chapter.

clear understanding of the subject to grasp at the outset this more limited meaning of the term. Energy which is stored in a system, even that part of it which is due to the molecular motions, is not to be associated with the term "heat." When energy is *transferred* from one system to another through the agency of chaotic molecular motion, then it is heat in the thermodynamic sense. Energy transferred by radiation is also commonly regarded as heat because like heat it does not involve action against an external force and the result is essentially the same. In other words, heat is a form of energy *in transition* from one storage system to another. We shall endeavor to use the term in this limited sense and avoid much of the confusion that has arisen from the common loose definition of heat in thermodynamic discussions.

Heat Reservoir.—This is a common term in dealing with heat engines but somewhat inconsistent with the ideas just advanced. Strictly, heat is always in transition and is never stored in a reservoir. The term refers to any mass that can transfer or receive energy in the form of heat (or radiant energy equivalent to heat) to or from another system. It will be convenient in certain thermodynamic arguments to imagine very large heat reservoirs, typified by the ocean or the atmosphere, to or from which finite quantities of heat may be transferred without any appreciable effect on the temperature.

Adiabatic Process.—We shall have frequent occasion to consider changes in which no exchange or transfer of heat occurs between a system and its surroundings. Such a process is designated as "adiabatic." It can only occur if (1) no temperature difference exists or (2) the system is thermally insulated from the surroundings. Since no known substance is a perfect heat insulator, we can approach only more or less closely to a true adiabatic process in this way. By controlling the temperature of the immediate surroundings so that it always equals (within limits, of course) that of the system, a very close approach to an adiabatic process can be realized.

Quantitative Definition of Heat.—Quantity of heat may be defined in terms of its effect in changing the temperature of some substance to which it is transferred. The substance commonly chosen is water; since the heat quantity necessary to raise the temperature of unit mass by a given amount is not the same at all temperature levels, the temperatures should be specified where high accuracy is required. The units of heat in common use are the calorie, the British thermal unit (B.t.u.), and the centigrade heat unit (c.h.u.) or pound centigrade unit (p.c.u.). The gram-calorie is the quantity of heat necessary to raise the temperature of 1 g. of water by 1°C. It is a 15° cal. if the temperature range is 14.5 to 15.5°C. The mean calorie is one-hundredth of the amount of heat necessary to raise the temperature from 0 to 100°C. The B.t.u. is simi-

larly defined on the basis of 1 lb. of water and 1°F., and the c.h.u. on the basis of 1 lb. and 1°C. In the case of the latter two units, no distinction is usually made between the mean unit based on the temperature change from 32 to 212°F. and the unit based on a more limited temperature change.

There has been a movement in recent years toward defining heat units more or less arbitrarily in terms of other energy units, especially electrical units. For example, the international kilogram-calorie is defined as $\frac{1}{860}$ international kilowatt-hours, or the gram-calorie as 4.1833 international joules. This makes 1 B.t.u. equal to 0.293019 international watt-hours or 778.26 ft.-lb. The basis for such a definition will be clearer after the next chapter has been read. The reason for it is to avoid basing the unit on some property of matter that is subject to revision in its value. This is more important in scientific than in engineering work. Furthermore, in modern calorimetry, heat quantities are directly measured in electrical units, and hence it is more convenient to define them on such a basis. The choice of numerical values could be entirely arbitrary, but naturally it was desirable to choose them so as to change as little as possible the size of the units already in use.

Heat Capacity and Specific Heat.—The addition of heat to a substance frequently results in a temperature rise whose magnitude depends on the mass and on a specific property of the substance. We may express this for a differential change of temperature by the following equation:

$$dQ = mc\, dt \qquad (I.30)$$

where Q = quantity of heat.

   m = mass.

   c = a constant, characteristic of the substance *and of the manner* in which the heating takes place.

c is called the "specific heat" and is defined by this equation. The product mc will be called the "heat capacity," and if m is the molecular weight it is molal heat capacity.[1]

It should be clear from the preceding discussion that heat is not a *property* of substances and no more is C. That is, the value of C depends on the particular way in which the system is heated. If the pressure on it is held constant, then C is represented as C_p, or the specific heat at constant pressure. Likewise, we may define a specific heat at constant volume C_v. Both these quantities are properties, as will be evident from the discussion in Chap. III. Many other specific heats are possible but not in common use though at least one other will be defined in a later chapter. Let it be emphasized again that specific heat in general is not a

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[1] Since molal heat capacity will be used so much more frequently than specific heat and since by common usage it is generally called "specific heat," we shall represent it by C instead of Mc.

property in the usual meaning of the term but merely a quantity defined by the above equation. However, once a definite path, such as at constant pressure, has been specified, then that particular specific heat *is* a property of the system.

The c defined by Eq. (I.30) may be called the "instantaneous specific heat," a quantity not capable of direct measurement by thermal means. (It can, however, be directly determined from a measurement of the velocity of sound.) We measure a mean specific heat defined by the equation

$$c_m = \frac{Q}{m(t_2 - t_1)} \tag{I.31}$$

where $t_2 - t_1$ is a finite temperature range. The relation between these two specific heats is given by the equation

$$c_m = \frac{\int_{t_1}^{t_2} c \, dt}{t_2 - t_1} \tag{I.32}$$

Specific heat has units of heat quantity divided by mass times temperature. From this it follows that 1 B.t.u. per lb. per °F. = 1 g.-cal. per g. per °C. = 1 c.h.u. per lb. per °C. Since heat can also be expressed in other energy units we may express c (for example) as joules per gram per degree centigrade. 1 g.-cal. per g. per °C. = 4.183 joules per gram per degree centigrade.

The instantaneous specific heat at constant p or constant V is a function of the temperature, and for most practical purposes the function is commonly represented by the simple power series

$$C = \alpha + \beta t + \gamma t^2 + \delta t^3 + \cdots \tag{I.33}$$

Since this is a purely empirical equation it must not be extrapolated beyond the range for which the constants were determined. Failure to observe this precaution has led to many erroneous conclusions.

Latent Heat.—In certain cases the addition of heat to or the extraction of heat from a system results in no temperature change. This is true, for example, when a phase change occurs for a pure substance at constant pressure. Such heat is known as "latent heat." Common examples are heats of vaporization, fusion, and sublimation. Heats of chemical reaction are also latent heats since they are commonly associated with isothermal conditions. Such heats are expressed as B.t.u. per pound or gram-calories per gram or per gram-mole.

1 g.-cal. per g. = 1 c.h.u. per lb. = 1.8 B.t.u. per lb.

SPONTANEOUS, OR IRREVERSIBLE, PROCESSES

All naturally occurring changes or processes are irreversible in the sense that they tend to proceed in a certain direction and never, when

left to themselves, to reverse, or go in the opposite direction.   Like a clock they tend to "run down" and cannot "rewind" themselves. Familiar examples are

1. Transfer of heat by conduction and convection with a finite temperature difference.

2. Expansion of a gas from a high to a low pressure through a throttle.

3. The mixing of two gases.

4. A waterfall.

5. A chemical reaction such as the combustion of hydrogen.

The fact that a mixed gas does not spontaneously unmix or that water will not spontaneously decompose at room temperature to oxygen and hydrogen or that heat always flows from a higher to lower temperature— all these are matters of common experience, and it seems almost absurd to make such obvious statements. Nevertheless, the second law of thermodynamics is nothing more or less than a generalized statement of such common experience, and in order to grasp its meaning it will be necessary to consider in some detail the relation between an actual, or irreversible, process and an idealized process, which will be called the "reversible process."

All the above changes *can* be reversed.   Thus, we can transfer heat from a region of low temperature to one of higher temperature, we can separate a gas mixture into its components, we can cause water to flow uphill, and we can decompose water at room temperature into hydrogen and oxygen.   The important point is that we can do these things only at the expense of some other system, which itself becomes run down. Work must be done to reverse these changes, and the work can be obtained only by allowing a spontaneous change to occur somewhere else.   To state this another way, we can undo the result of a given spontaneous change only by allowing another such change to occur.

Only when the tendency for a spontaneous change exists can we secure useful work.   It is somewhat paradoxical that the change cannot be entirely spontaneous and irreversible if we are to employ it for useful work, but the tendency for spontaneous change must exist.   Thus, if we consider a large body of water at uniform temperature, there is no tendency for any flow of heat to occur and we are unable to obtain any work from it although the body possesses a large store of energy.   If, however, different portions were at different temperatures, then there would be a tendency for spontaneous change—*i.e.*, the temperatures would tend to equalize.   By providing a suitable mechanism we can utilize the tendency for spontaneous change to secure work; and in so doing we really prevent the change from being entirely irreversible, and we can, in fact, imagine it to be reversible at the limit.

Tendency to change we recognize as being due to certain "driving forces," and this concept is encountered in considering almost all the

unit operations and processes of chemical engineering. The driving force for heat transfer is a temperature difference, for material transfer it is a concentration difference, and for fluid flow a pressure difference. Whenever there is such a driving force, there is a tendency for change. The change may not appear to take place because of some resistance that may so slow up the change as to make it imperceptible. If we can recognize the existence of the driving force, then we can predict the direction of the change and we know also that useful work can be obtained. In the case of heat transfer, fluid flow, and other such purely mechanical processes, the driving forces are easily recognizable, but this is no longer true in the case of chemical systems where the driving force may be a more elusive quantity. To deal with such cases, special functions such as "free energy" have been devised, about which more will be said in a later chapter.

EQUILIBRIUM AND THE REVERSIBLE PROCESS

True Equilibrium.—The end point of any spontaneous process is a state of equilibrium in which forces are balanced and there is no further tendency to change, no driving force. It is important to make a distinction between a true, or stable, equilibrium with its balanced forces and an apparent, or false, equilibrium in which a *tendency* to change still exists but, owing to a high resistance, the rate of change is so small that to all intents and purposes no change is taking place. The distinguishing test is a simple one. In a true equilibrium, since the forces are balanced, a slight (strictly, infinitesimal) increase or decrease of one of the forces will cause a shift in the position of the equilibrium. For example, imagine a piston in a vertical cylinder with fluid pressure acting on the bottom of the piston and balanced by weights placed on top of the piston. A practical case is the well-known dead-weight piston gauge used for pressure measurement. In the absence of any friction, a very small weight added to those on the piston will cause it to move down. The motion may be very slow and sensitive devices might be needed to detect it, but it exists. If now the fluid pressure is increased ever so slightly, the downward motion can be arrested and a further slight increase reverses the direction of motion. The presence of considerable friction between the piston and the cylinder wall will make it necessary to place a much larger weight on the piston to cause a definite downward motion or to make a proportionately much greater increase in fluid pressure to reverse the direction of motion. In this case, cessation of motion does not indicate a true equilibrium. Actually, of course, the friction cannot be entirely eliminated, and so we never reach a true state of equilibrium; but by careful choice of conditions we can approach it quite closely, and it is only a slight extrapolation to imagine the true equilibrium state.

The true equilibrium state is, like the ideal gas, a concept and not a real state encountered in practice; nevertheless, it is a concept of great practical utility in the study of actual changes.

Let us consider one other example where the forces are chemical rather than purely mechanical. If gaseous oxygen and hydrogen and water vapor are mixed at room temperature, no detectable change in the composition of the mixture occurs no matter how long they are allowed to stand. Nevertheless, this system is not in chemical equilibrium. The tendency toward change exists, but it is enormously retarded by something analogous to friction in a mechanical system. The falseness of the equilibrium can be demonstrated in various ways. Add a small amount of hydrogen or oxygen, and if the system were in true equilibrium a reaction resulting in the formation of more water vapor would occur. Actually, the addition neither of water vapor nor of hydrogen causes any reaction to occur; on the other hand, if only a (relatively) minute amount of energy is introduced in the form of an electric spark, a rapid displacement of considerable amplitude may occur, showing that the tendency toward considerable change did exist. If the same system were considered at a temperature of 2000°C., the situation would be entirely altered. Small additions of either hydrogen or water vapor would cause an immediate reaction, and the use of the spark would have no appreciable effect. We have, therefore, a definite criterion of a true equilibrium; and in the experimental investigation of equilibria it is always well to approach the equilibrium from both directions to avoid being deceived by false equilibria.

A system in equilibrium is said to be in a "stable state"; conversely, a nonequilibrium system is an "unstable" one. Thus, water can be cooled below 0°C. at the pressure of 1 atm., but this is not the stable form of the chemical substance H_2O under these conditions. Solids, because of the resistance to internal rearrangements inherent in their structure, may exist for long periods in essentially unstable forms. A familiar example is glass, which is an unstable system from the thermodynamic point of view.

Partial Equilibrium.—One frequently, or perhaps usually, has to deal with "partial equilibria," particularly in the case of chemical reactions. By a partial equilibrium is meant one in which true equilibrium is reached with respect to one particular change but not with respect to other possible changes. We may deal with the equilibrium solubility of hydrogen and oxygen in water under such conditions that the system is far from being in chemical equilibrium. The rate of approach to the chemical equilibrium is so exceedingly slow as compared with that of the solubility equilibrium that it can be entirely disregarded. This is an extreme case. There are many cases, especially in dealing with organic chemical reac-

tions, where the question is of importance. For example, suppose one wished to determine the equilibrium point in the reaction

$$CO + 2H_2 = CH_3OH,$$
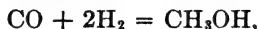
at a given pressure and temperature. The chief difficulty lies in the fact that so many other reactions can occur simultaneously. To cite only a few,

$$CO + 3H_2 = CH_4 + H_2O$$
$$CO + H_2O = CO_2 + H_2$$
$$2CH_3OH = (CH_3)_2O + H_2O$$
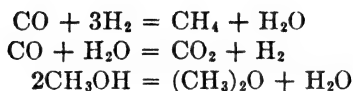
In general, we are not interested in a complete equilibrium with respect to all possible reactions, which would be quite a different thing from the partial equilibrium with respect to the methanol synthesis reaction, the others being entirely suppressed. Unless the rates of the other, or "side," reactions are substantially zero, we cannot reach a true equilibrium in the main reaction. Practically, all that we can hope to do is so to choose conditions as to minimize as far as possible the rates of the side reactions. We may in this way achieve a close enough approach to true equilibrium in the one reaction for all practical purposes.

Equilibrium and the Driving Force.—Although we have emphasized the point that thermodynamics is concerned with equilibrium states and not at all with rates of change, nevertheless there is an important link between equilibrium and rate through the driving force. The rate at which any change proceeds is, in general, conditioned by the distance from an equilibrium state, and therefore it becomes necessary to have a knowledge of equilibrium states in order to determine driving forces. Thus, in order to calculate the size of an absorption tower we must be able to calculate the mean driving force, which will be a difference between the actual concentration of the solute and its equilibrium concentration. Similar considerations apply in heat transfer, in drying, in chemical reactions, and, in fact, in most of the processes with which the chemical engineer is concerned.

The Reversible Process.—So far we have been considering isolated, unconnected equilibrium states and have seen that *reversibility* is a criterion of equilibrium. If now we consider a connected series of equilibrium states, each representing only an infinitesimal displacement from the adjacent one but with the over-all result a finite change, then we have a *reversible process*. All actual or spontaneous processes can be made to approach more or less closely to a reversible process by suitable choice of conditions; but, like the absolute zero of temperature and the ideal gas, the strictly reversible process is purely a concept that aids in the analysis of certain problems. However, the approach of actual

processes to this ideal limit can be made almost as close as we please. The closeness of approach is generally limited by economic factors rather than purely physical ones. The truly reversible process would require an infinite time for its completion, but we are generally in a hurry and require that our processes complete themselves in as short a time as possible.

Reversible Transfer of Heat.—Earlier in this chapter certain irreversible processes were considered. Let us now consider the reversible execution of these same processes. Instead of allowing heat from a reservoir at t_1 to flow spontaneously by conduction to another reservoir at a lower temperature t_2, the heat can be allowed to flow to a gas confined under pressure by a piston the force on which is balanced against another force imposed by a mechanism doing work. The gas is then allowed to expand, its temperature being maintained constant by heat transfer from the reservoir at t_1. To secure such a transfer the temperature of the gas must be slightly less than that of the reservoir but the difference can be as small as we please as long as we are not concerned about the speed at which the process occurs. If the difference is an amount dt, then an infinitesimal increase in the gas temperature will arrest the flow and a further infinitesimal increase will reverse it. In other words, this is the necessary and sufficient condition for the reversible execution of the process.

As the gas expands, its pressure drops and the balancing force acting back through the piston rod must also decrease. We shall not consider in detail the mechanism for accomplishing this. Suffice it to say that it can be done with the aid of a flywheel. From what has been said before it should be clear that the necessary condition for the reversibility of the process is that the force from the work-doing mechanism should at all times be only an infinitesimal amount less than that due to the gas pressure.

At some point in the stroke of the piston, let us remove the cylinder from contact with the heat reservoir and insulate it thermally from the surroundings. As the expansion continues, the temperature of the gas will decrease (adiabatic expansion). When the temperature has decreased to t_2, the cylinder should be placed in contact with the reservoir at t_2 and the direction of motion of the piston reversed by maintaining the force acting through the piston rod from the flywheel mechanism slightly greater (an amount dp in terms of pressure) than the force due to gas pressure. The gas is thus compressed isothermally, the constant temperature being maintained by the transfer of heat to the reservoir at t_2. The cycle of operations may be completed, leaving the system in readiness to receive more heat from the reservoir at t_1, by again insulating (thermally) the cylinder from the surroundings and causing the gas to be

compressed to the initial pressure while at the same time the temperature increases to t_1 (adiabatic compression).

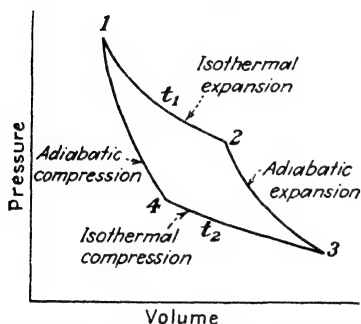The cycle of changes to which the gas was subjected may be represented on a pV diagram as in Fig. I.4. Step $\overline{12}$ is the first isothermal expansion while the gas in the cylinder receives heat from the reservoir at t_1. Step $\overline{23}$ is the adiabatic expansion, $\overline{34}$ the isothermal compression, and $\overline{41}$ the adiabatic compression. The net result of the process has been the transfer of a certain quantity of heat from the reservoir at t_1 to that at t_2; but at the same time some work has been done against external forces, which was not the case when the transfer of heat occurred by direct conduction from one reservoir to the other. One other difference between the two transfer processes should be noted. In the case of the reversible process, the quantity of heat given up to the reservoir at t_2 is less than that taken in from t_1 by an amount equivalent to the work done.

FIG. I.4.—Cycle illustrating reversible heat transfer.

The cycle of changes we have just considered is typical of the changes that occur in heat engines. In general, a heat engine is defined as any mechanism that converts heat into work. In the idealized heat engine whose cycle was considered in the above discussion, we purposely avoided consideration of details of mechanism because they would serve only to confuse the argument and interfere with a clear understanding of the fundamental principles. This is the usual procedure in most thermodynamic discussions.

If the opposing forces on the piston are in balance except for a differential amount and if the reservoirs never differ more than a differential amount in temperature from the gas in the cylinder, then a very slight change in one of the temperatures or one of the pressures will serve to reverse the direction of the process and we can equally well use it to convey heat from t_2 to t_1. Since the conditions are everywhere the same for the reverse process as for the forward process (within a differential amount), then the work which would be required from the mechanism to convey heat from t_2 to t_1 is exactly the same (for the same amount of heat at each reservoir) as that which would be delivered to it when the heat transfer is in the opposite direction. This means that if we allowed the process to operate through several (or any number of) cycles conveying heat from t_1 to t_2 and used the work done to store up energy in a form such that it could be readily and completely reutilized—we may symbol-

ize this by the raising of a weight—then, by allowing the weight to fall, we could restore the reservoirs to their original state by means of the stored energy. This is an important principle. Generalized, it means that any completely reversible process will yield sufficient energy in a readily available form (*i.e.*, as work) so that all conditions in the system can be restored to their original values without calling on any outside system.

Degree of Irreversibility.—We have been considering a process carried out in two extreme, or limiting, ways, the one completely irreversible and the other completely reversible. An infinite number of gradations in between these limits is possible. That is, there are various degrees of reversibility or irreversibility, and it is important to recognize this fact in speaking of irreversible processes.

To consider again our simple heat-engine cycle of Fig. I.4, the gas in the cylinder during stroke $\overline{12}$ could be at t_1', lower than t_1 by a finite amount Δt, or the pressure in the gas during the same stroke might be less by an amount Δp than the force acting through the piston rod divided by the area of the piston. Either of these conditions would result in a smaller area enclosed within the cycle for the same amplitude of change. Since the enclosed area, as we have already shown, is a measure of the work, any irreversible effect such as a finite Δp or Δt will result in less work gained (or more work required for the process operating in the opposite direction). Therefore, the completely reversible process is the one that will deliver the maximum amount of work (or require the minimum) for a given set of conditions.

The Reversible Process as a Standard of Comparison.—The preceding leads us to the reason for the importance of the concept of reversibility and the reversible process in thermodynamics. Admittedly, the reversible process is an idealized process that cannot be attained in practice. This should be clearly understood. In the process we have just been considering, reversibility implies the absence of all friction, materials that do not conduct heat, and an infinitesimal rate of execution (since only infinitesimal driving forces are allowed). Practical economic operation may require a considerable departure from these idealized conditions; but there is no inherent physical difficulty that prevents us from choosing conditions so as to approach very closely to this ideal, and a slight extrapolation carries us to it. The sole reason for the invention of the concept of the reversible process is to establish a standard for the comparison of actual processes. The reversible process is one that gives the maximum accomplishment, *i.e.*, yields the greatest amount of work or requires the least work to bring about a given change. It tells us the maximum efficiency toward which we may strive but which we never expect to equal. Without such an absolute standard or yardstick the attempts of engineers to improve processes would be purely shots in the dark with no goal at

which to aim. With the reversible process as our standard we know at once whether an actual process is already highly efficient or whether it is very inefficient and therefore capable of considerable improvement.

The concept of the reversible process is of the greatest value in the analysis of any complex process consisting of a number of steps. One who has learned to recognize the common irreversible effects can immediately identify the sources of inefficiency, for it is axiomatic that every irreversible change means a loss of useful effect and hence a decrease in efficiency. Many examples of this will be given in later chapters.

Reversible Gas Expansion.—We have digressed from the task we started some pages back, which was to consider the reversible execution
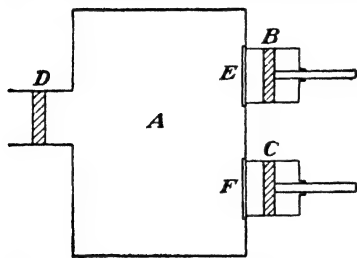

FIG. I.5.—Reversible mixing of two gases.

of the spontaneous processes mentioned on page 27. After the detailed treatment of the first only a brief discussion need be given the others. The reversible execution of a gas expansion came into the simple heat-engine process and needs no further discussion. It may be pointed out in passing that the adiabatic expansion of a real (as distinct from ideal) gas through a porous plug or a throttle with the performance of no usable external work is not a wholly irreversible process, as is sometimes thought; for it results in a temperature change, which may be utilized to obtain work in a heat-engine cycle as just outlined, and this may be utilized to recompress the gas partly.

Reversible Mixing of Gases.—When two gases are brought into contact and allowed to mix by diffusion, the process is irreversible because there is no possible way of separating the mixture without enlisting aid from some outside source. The reversible mixing (or separation) of gases is readily accomplished (in imagination) by the use of the semipermeable membrane, *i.e.*, a membrane completely permeable to one gas and absolutely impermeable to all others. This is an idealized piece of apparatus like the frictionless piston and the nonconducting solid; but actual membranes have been prepared that closely approach the ideal (for example, membranes used in the study of osmosis and thin palladium foil, which is remarkably permeable to hydrogen and only slightly so to other common gases), and again it is only a slight extrapolation to the limit, *i.e.*, the perfect membrane.[1]

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[1] Any system of a salt hydrate in contact with a moist atmosphere is a good example of something that has the filtering property of a semipermeable membrane. Water vapor can readily pass the gas-solid interface, but not the other components of the gas.

Consider a reservoir A (Fig. I.5) containing an equimolal mixture of gaseous oxygen and nitrogen at 1 atm. pressure. Let D be a cylinder containing a piston exposed to atmospheric pressure whose only purpose is to increase the volume of A as gas is added, in order to maintain the pressure constant. Cylinders B and C contain oxygen and nitrogen, respectively, and are provided with pistons connected to suitable mechanisms for balancing the gas pressure at all points in the stroke. The spaces to the right of the pistons are complete vacuums. E and F are removable shutters, which can be replaced by semipermeable membranes when desired. All gases will be considered ideal for the sake of simplicity, but this restriction does not affect the principle involved. The whole apparatus is assumed to be surrounded by a constant-temperature bath acting as a heat reservoir.

At the start of the process, B and C are filled with gas at 1 atm. pressure, and the impermeable shutters are in place at E and F. Allow each gas to expand isothermally and reversibly to a pressure equal to its partial pressure in the reservoir. Then replace the shutters by the semipermeable membranes, one permeable only to oxygen and the other to nitrogen, and push each gas into A at constant pressure. Owing to the semipermeable nature of the membranes, the pressure opposing the injection is only the $\frac{1}{2}$ atm. partial pressure of the gas to which the membrane is permeable. The process can be reversed at any part of its cycle by an infinitesimal change in forces, or the net work gained from mixing a given quantity can be utilized to unmix an equal amount of gas.

Reversal of Waterfall.—The waterfall can be made reversible by diverting the high-level stream to a pipe, which conveys the water to a turbine situated at the lower level. In the turbine the water under pressure is caused to flow through suitable nozzles, which convert its potential energy to kinetic energy, which is in turn converted to kinetic energy of a rotating wheel. This energy may be stored for later use or used directly to reconvey the water to its original level provided that each step has been carried out in a reversible manner, *i.e.*, without friction.

Reversible Chemical Reaction.—Even the chemical reaction can be carried out in a reversible manner if a suitable mechanism is provided, which in this case may be a galvanic or electrochemical cell. Without going into a detailed consideration of such cells, it may be stated that most reactions that take place between ions can be made to yield an e.m.f. between two electrodes, and if this is opposed by an external e.m.f. the reaction can then be carried out in a reversible manner. A practical illustration of a reversible cell reaction is seen in the use of a standard cell in a potentiometer circuit. It is essential that this cell behave in a substantially reversible manner if it is to act as a standard of e.m.f.

Even certain gas reactions, such as the one already considered as an irreversible process, can be made ionic by choice of suitable material for the electrodes.   Thus hydrogen and oxygen can be irreversibly combined by ordinary combustion or reversibly combined in an electrochemical cell with an opposing e.m.f. less by a differential amount than the e.m.f. of the cell.   If the opposing e.m.f. is raised slightly, the reaction will be reversed, water decomposing into hydrogen and oxygen.   In the practical operation of such a cell, as in the case of all the other processes considered, certain irreversible effects are unavoidably present that lower the e.m.f. available for external work when the reaction proceeds in the direction to form water or raise the e.m.f. necessary to cause decomposition above the value for the ideal, reversible case.

A chemical reaction between gases, for example the reaction

$$3H_2 + N_2 = 2NH_3,$$
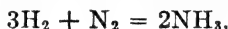
can be carried out reversibly—in imagination—by means of the mechanism already used to illustrate the reversible mixing of gases.   In Fig. I.5, the reservoir A, called an "equilibrium box" by van't Hoff, who devised this scheme, is assumed to contain a mixture of N_2, H_2, and NH_3 in equilibrium at some given pressure p and temperature t, both of which are to remain constant.   Cylinders B, C and D contain, respectively, H_2, N_2, and NH_3 all at some given pressure p_o, and impervious shutters keep them out of contact with the gases in the box.   Note that D is now considered to be a cylinder with piston connected to a work mechanism just as B and C.   As in the mixing of gases, the H_2 and N_2 are expanded isothermally and reversibly from their initial pressures to such pressures that they will be in equilibrium with the mixture in the box through semipermeable membranes (for ideal gases the pressure would be the partial pressure of the respective gas in the box).   The impervious shutters are then replaced by the semipermeable membranes as before and the gases injected into the box.   Since this will disturb the equilibrium in the box, NH_3 will be formed and as fast as it forms will be withdrawn into D through a semipermeable membrane.   In this way the composition in the box always remains the same.   Finally, the ammonia may be isothermally compressed from the partial pressure at which it exists in the box to p_o.   The net result has been the conversion of a given amount of N_2 and H_2, each at pressure p_o, to NH_3, also at p_o, by an isothermal process.   That the process is reversible may be seen by applying the usual criterion.   The question of the net work in such a process will be considered in a later chapter.   There are, of course, certain heat effects associated with the operation of the box.   During the compressions, heat must flow from the gas to the surroundings, and there will be a heat effect accompanying the reaction in the box that may be either plus or minus.

As long as these heat transfers take place between the system and a surrounding constant-temperature bath differing only dT in temperature, the transfers will be reversible.

Note on the Reversible Process.—This is a very difficult concept to define, and the beginner need not feel discouraged if he does not grasp the idea at once. In fact, it is practically impossible to define a reversible process in a way that does not raise more questions than it answers. Nevertheless, the concept is a useful one and it is the author's belief that the most satisfactory way to gain a workable knowledge of the concept is through some of the applications to be discussed in later chapters.

A brief glance behind the scenes at some of the difficulties that arise when one attempts to adhere too rigidly to any formal definition may be useful. Consider the expansion of a gas behind a piston with the force exerted by the gas always balanced by the opposing force in the piston rod. Such a process would be reversible by one of the criteria that was given for a reversible process, but suppose that the force of the piston rod were entirely dissipated as heat by allowing it to drive a water brake. By another of the criteria given above, the process as a whole is clearly irreversible, for there is no way of recompressing the gas without calling on aid from an outside system.

Now go a step further, and suppose that gas confined in a storage cylinder expands through a throttle to a lower pressure. As a whole, this process is certainly irreversible, but as far as the gas in the cylinder is concerned it makes no difference whether it is pushing against a piston or merely against other gas molecules. Consequently, the state change of the gas in the cylinder can be treated by the equations that have been derived for equilibrium or reversible processes.

Let us take another simple illustration from the field of heat transfer. Suppose a fluid is being heated from 80 to 200°F. by flow in an exchanger countercurrent to a fluid that cools from 250 to 100°F. Either the heating or the cooling by itself can be regarded as a reversible change and is commonly so treated in the usual thermodynamic discussion. In order to preserve the idea of heat flow under an infinitesimal temperature difference being the only way it can occur reversibly, it is necessary only to invent in imagination a special heat reservoir whose temperature always remains dt degrees above (or below) that of the fluid being heated (or cooled). On the other hand, there is no ambiguity about the process as a whole. It is clearly an irreversible one because the heat is transferred through a finite Δt.

Another point of view on the reversible process will be found useful in certain arguments and will be presented briefly. Since it represents a succession of equilibrium states each only a differential step from its neighbor, the reversible process can be represented as a continuous line

on a state diagram (*pv* or *pt*, etc.).   On the other hand, the irreversible process cannot be so represented.   One can note the terminal states and indicate the general direction of change, but it is inherent in the nature of the irreversible process that the complete path of the change is indeterminate and therefore cannot be drawn as a line on a thermodynamic diagram.

CHAPTER II

THE FIRST TWO FUNDAMENTAL LAWS

Historical.—The first (though very crude) attempt at any kind of quantitative measure of the relation between heat and other forms of energy was the experiment of Count Rumford.[1] He rotated by horsepower a gun-metal cylinder with a blunt boring tool pressed against it and measured the increase in temperature and the amount of metal rubbed off. He showed in this way that the quantity of heat given off was inexhaustible and depended only on the continued operation of the experiment. The amount was so great and the quantity of matter rubbed off so small that there could be no relation between them. He concluded from his experiments that heat could not possibly be a material fluid but that it must be motion. This was the beginning of the downfall of the caloric theory of heat.

The experiments of Davy about the same time on the melting of ice by friction were also quite inconsistent with the caloric theory and led to the conclusion that heat is due to the motion of small particles and that this motion can be generated by the process of rubbing.

In spite of these experiments many scientists still clung to the old caloric theory and it remained for the beautifully executed quantitative experiments of Joule from 1840–1850 to establish firmly the new theory. There was no escape from the exact figures that Joule assembled. He showed that, whenever mechanical or electrical work was done under conditions such that no storage of energy occurred in the system, a quantity of heat was generated which always bore a fixed ratio to the work done, the ratio being dependent only on the units chosen. This was definite proof that heat is a form of energy. Other men before Joule had expressed correct ideas on the equivalence between heat and work and even given an approximate value for the equivalent, but their work was not so convincing as that of Joule owing to the paucity of experimental facts on which they based their arguments. Mention should be made however, of the Austrian physician Mayer, who expressed remarkably clear ideas on the subject in 1842.

The idea that energy is conserved, *i.e.*, can be neither created nor destroyed, was already well established by physicists in dealing with

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[1] RUMFORD, COUNT, BENJAMIN THOMPSON, An Inquiry Concerning the Source of the Heat Which Is Excited by Friction, *Phil. Trans.*, **88**, 80–102 (1798).

purely mechanical systems.   The extension of this principle to include other forms of energy constitutes the first law of thermodynamics.

Whereas the first law was essentially a deduction from experiment, the second law had its beginnings in almost pure inductive reasoning. Nicolas Léonard Sadi Carnot, a young French military engineer, set himself the task of reasoning about the maximum amount of work that can be obtained from a given quantity of heat in a heat engine.   His "Reflections on the Motive Power of Heat and on Machines Fitted to Develop That Power," published in 1824, contains his famous principle (still the fundamental basis for all discussion of heat engines) that the efficiency of a simple, ideal heat engine depends only on the temperatures of the source of heat and the refrigerator (the reservoir to which heat is rejected) and is entirely independent of the mechanism or the working substance employed.   Carnot's proof of his theorem was based partly on the old caloric, or material, theory of heat, which was entirely overthrown by the work of Joule.   It remained for Lord Kelvin in Scotland and Clausius in Germany to show independently that Carnot's principle was still valid on the basis of the new theory of heat.   The axioms that they stated to make Carnot's proof valid still form the commonly accepted short statements of the second law.   At this time, Clausius introduced the function "entropy," which, though the bane of all beginning students of thermodynamics, had a most far-reaching effect on the quantitative development of the second law and may be said to be indispensable in its application.

The second law was accepted with reluctance by the scientific world and doubts were expressed as to its validity even in very recent years.   It now rests, however, on a very firm and broad base of experimental fact and engineering experience and can be accepted as an absolutely rigorous law without a single exception.   Since the time of Carnot, Kelvin, and Clausius, it has been greatly broadened in its application beyond the field of heat engines; in fact, it may be said to underlie almost all physical phenomena.   It will be possible to mention but one of the pioneers who contributed to this later development—Josiah Willard Gibbs, mathematical physicist of Yale University, to whom we owe the fundamentals of most of the applications of thermodynamics to chemical systems.

THE FIRST LAW AND THE CONCEPT OF ENERGY

Work Equivalent of Heat.—If we take any static (*i.e.*, nonflowing) system, no matter how complex in composition it may be, and put it through a *cycle* of changes during the course of which work is done on the system by forces acting from the surroundings, or vice versa, and heat is transferred to (or from) the system from (or to) the surroundings, then it is found by experience that a very simple relationship holds between

the algebraic summation of all the work effects (each force causes a work effect) and the summation of all the heat effects, *viz.*,

$$\Sigma W = J \Sigma Q \tag{II.1}$$

For the moment, we shall assume all the work effects to be of one kind, *i.e.*, all mechanical work or all electrical work, so that all are measurable in the same units. The heat effects are of course to be measured in thermal units, such as calories or B.t.u., since their measurement in any other units involves the very principle that we are illustrating.

This simple generalization is the direct result of the experiments of Joule already mentioned, but the value of the proportionality constant J has been much more accurately determined by later investigators. It depends *only on the units* chosen to measure W and Q and in no way on the system chosen or on the mechanism employed or any other variable. When the work is mechanical, it is known as the "mechanical equivalent of heat." Similarly, we may have an "electrical equivalent of heat." Since experiment also shows that there is a similar equivalence between the different kinds of work (for example, an electrical equivalent of mechanical work), we may remove the restriction that the work effects should all be of one kind since the various kinds are readily interconvertible. (This fact will be implied in all subsequent treatment.)

Concept of Energy Content.—The relation expressed by Eq. (II.1) is strictly true only when the working substance or the system with which we are experimenting passes through a complete cycle of changes—*i.e.*, returns to its original condition. If one considers any process such as the vaporization of a liquid or a chemical reaction or compression of a gas, there is no simple, universal relation between the external heat and work effects. Since both heat and work are the external effects resulting from changes within a system and since these effects must be considered as arising from something already existent, or, in other words, must have a cause, the concept of energy has been invented for this purpose. Heat and work are to be regarded as forms of energy and more particularly in the thermodynamic sense as the external manifestations of stored energy. Whenever heat and work are not equivalent, as is generally the case in any noncyclic process, we account for this fact by saying that a quantity of energy has been stored in the system or, conversely, that some stored energy has been removed from the system and appears as heat or work or both. Energy is something that may either be stored in a system or passed freely from one system to another in the form of heat or work, but it is always *conserved*. In all its transformations it remains absolutely unchanged in amount. This is the principle of the conservation of energy, which forms the basis of the first law of thermodynamics, and it rests primarily on the experimental facts generalized by Eq. (II.1).

Energy stored in a system is a definite property of the system and is represented by the symbol E. It is sometimes called "energy content" or "internal energy" to distinguish it from energy that may be associated with a system but not a property of it. We shall adopt the former term. The energy content we shall represent by E is that due to the configuration of the ultimate particles of the matter composing the system and to their motions. Energy due to mass motion of the system as a whole (dynamic as distinct from static system) or to its position in a gravitational, electric, or magnetic field is not included in the quantity E, as these forms of energy are not properties of the system. A given system under a given set of conditions has a certain energy content; this implies that whenever the system, after a series of changes, returns exactly to its initial condition, the energy content is just the same as it was before. It also implies that, under another set of conditions, it will have a different energy content. While this is true in general, it is not necessarily so. For example, an ideal gas, as will be shown later (page 100), has the same energy content at a given temperature, *regardless of the pressure.*

Mathematical Statement of First Law for a Nonflow System.— Equation (II.1) may now be broadened to include these ideas:

$$\Delta E = J\Sigma Q - \Sigma W \qquad (II.2)^{1}$$

where ΔE, the change in energy content of the system, is really defined by the equation. For a cyclic process, $\Delta E = 0$, and the equation reduces to Eq. (II.1). For a noncyclic process, it simply defines the difference between the heat effects and the work effects as being due to a storage in, or depletion of energy from, a system, in an amount characteristic of the initial and final states of the system.

It should be emphasized that we are concerned only with *changes* in the amount of energy and not the absolute amount of such energy about which little is known at the present time.

The equation implies that ΔE is measured in the same units as W. It could just as well be measured in heat units, in which case it should be multiplied by J. Since the ideas just discussed imply that all forms of energy are equivalent and interconvertible without loss, it is convenient to express all terms in Eq. (II.2) in the same units and omit J from all our thermodynamic equations. This is a simplification that we shall adopt with but few exceptions and those will be cases where it is desirable to emphasize the factor J. The statement of the first law as given by Eq. (II.2), sometimes referred to as an "energy balance" or as the "equation of energy," strictly applies only to a static system. For a dynamic, or

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[1] $\Delta E = E$ in final state $- E$ in initial state. Heat added to the system and work done by the system are taken to be positive.

flow, system two other energy terms are involved, as will be shown later, more especially in Chap. VIII.

Validity of the First Law.—For all ordinary phenomena and more particularly for those involved in engineering work, the first law may be regarded as completely valid within the limits of the most accurate measurements that scientists are able to make. However, it is interesting to note in passing that to explain certain subatomic and also stellar phenomena it has been necessary to give up the idea of energy conservation and postulate that energy may be created from matter, and vice versa. The relation between them is given by the relativity theory as $E = c^2 m$, where c is the velocity of light. Because c^2 is so large, enormous amounts of energy result from the destruction of minute amounts of matter. Thus 1 g. of any substance is equivalent to 25,000,000 kw.-hr., to obtain which by present methods of power generation would require the burning of about 12,500 tons of coal. No one, at the present time, has any definite idea of how to tap and control the enormous supply of energy that, according to this theory, is locked up as matter.[1]

Classification of Energy.—Energy is sometimes classified into various forms as expressed by the terms "potential," "kinetic," "mechanical," "chemical," "electrical," "atomic," etc. Such classification is apt to be more confusing than enlightening, but the terms are in common use and convenient for some purposes and hence deserve some mention. Potential energy is the energy that a system possesses by virtue of its particular configuration. The simplest case would be any object in relation to its position above the earth's surface. Work must be done to elevate any mass above the surface of the earth, and the energy represented by the work done is said to be stored in the system (*i.e.*, the combination of the mass and the earth) as potential energy—"potential" because it is capable of yielding work if the body is allowed to fall to the earth. Like all energy it has no absolute amount but is purely relative, depending on the choice of a datum plane.

Potential energy of a given system may also be "internal" owing to the particular configuration of the molecules, atoms, electrons, etc., of which it is composed. There are forces of attraction between the molecules of substances; and as the distance between them changes as in the expansion of a gas or the vaporization of a liquid, changes in potential energy occur analogous to that which occurs when a body changes position in the earth's gravitational field.

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[1] Recent work on the fission of the uranium isotope of atomic weight 235, in which relatively enormous energy releases (actually very small because of the minute amount of matter involved) have been measured, has raised hopes that a way may be found to unlock the stores of atomic energy. All this work is shrouded in deep secrecy at the present time owing to its potential importance in the war.

The pitfalls that the unwary may be led into by a too literal interpretation of some of these terms may be illustrated by the following case: When a gas is compressed isothermally from p_1 to p_2, the idea of potential energy leads, on first thought, to the conclusion that the gas at the pressure p_2 possesses a higher energy content than that at p_1 because it is capable of doing work by expansion. Such a view is quite erroneous as will be shown later (page 295); in fact, the reverse is true. The energy content of a gas decreases as pressure increases at constant temperature.

Kinetic energy is the energy associated with the motion of a body or particle relative to some reference body arbitrarily chosen. It is quantitatively defined for the simple case of a constant velocity by the well-known equation $K = \frac{1}{2}mu^2$, where m is mass and u is the relative velocity. Kinetic energy may be associated with the motion of large or tangible masses or with the motion of the ultimate particles such as molecules or atoms. All energy that is not kinetic is presumed to be potential.

Energy, whether potential or kinetic, that is associated with relatively large masses (as compared with the ultimate particles of which matter is composed) is generally referred to as mechanical energy. Energy associated with the motion or the relative positions of molecules is frequently called "thermal" or "heat energy." It should be recognized that this is purely a convenient descriptive term referring to any kind of stored energy that can be transferred to or from systems by virtue of temperature differences. It is not to be identified with a heat transfer Q.

Energy associated with e.m.fs. is called "electrical energy" and generally results from movements of the relatively mobile electrons that are present in varying degree in all substances.

When chemical reactions take place, potential energy is stored or released. The exact form in which this energy is stored is not known in detail; it must, of course, be related to the configuration of the atoms and electrons in the molecules. Since it is associated with chemical change, it is conveniently referred to as "chemical energy."

Atomic (or subatomic) energy is a form of potential energy whose origin is still a matter of dispute. It may be due to the forces acting between electrons and protons within the nucleus of the atom as distinct from those forces between the outer electrons of adjacent atoms which result in chemical reactions. As already pointed out, it may be due to the actual conversion of matter into energy. Whatever its source, its amount is extremely great, and all our other sources of energy are dwarfed in comparison.

We have no way of distinguishing the different forms of energy contained within a system. We cannot say that so much is chemical and so much is thermal or potential or kinetic. Consequently, all forms of

internal energy will be taken together and included in the single energy term E.

Transformation of Energy.—One seldom finds energy in just the form he wants it in for a particular purpose; it must be transformed. Obviously, it is important to get as large a proportion of the original energy as possible into the finally desired form, and a large part of the engineer's work is concerned with the factors affecting the efficiency of energy transformations. The particular province of the chemical engineer includes those transformations in which so-called "chemical energy" is involved. All chemical reactions involve a transfer of energy either from stored chemical energy to the surroundings as heat energy (exothermic reaction) or the reverse (endothermic). In many cases, the transformation is not the simple one from chemical energy to one other form but is more complex in that mechanical energy and also electrical energy may be involved. Thus, if a chemical reaction takes place in an electrochemical cell, some of the chemical energy may appear as heat given off to the surroundings, another portion, if there is a volume increase due to the cell reaction, as mechanical work done against the constant pressure of the atmosphere, and the major portion as electrical work.

Energy may pass through several transformations in series before it finally arrives at the desired form. The term "transformation chain" may be used to designate such a series of changes. For example, consider the following transformation chain: The chemical energy of a fuel is unlocked by the chemical reaction known as "combustion" and is transformed to heat energy in the products of combustion. This energy is then transferred as heat by conduction, convection, and radiation to energy in steam, which in turn is transformed to mechanical energy (work) in the steam engine or turbine. At this point, we may have some 20 per cent of the original chemical energy in the form of the mechanical energy of large masses in motion. We speak of the other 80 per cent as representing "losses." Actually, the energy is not lost but is merely in another form than the one desired and for reasons connected with the second law of thermodynamics may be "unavailable," *i.e.*, not capable of being transformed into any useful form. Most of the above 80 per cent is represented by energy still present in the steam after it has been used in the engine and discharged to the condensing system.

To continue the chain, the mechanical energy may be transformed to electrical energy by means of a generator and the electrical energy to chemical energy in a storage battery. Thus the over-all result has been a change from chemical energy in one system to chemical energy in another system, and the over-all efficiency of the transformation is not over 15 per cent at the best. This indicates that there is room for much

improvement in certain steps of such transformation chains; we shall deal with this in more detail in later chapters.

It would seem that this is a rather clumsy and roundabout way of getting from chemical energy in one system to the same form in another system. In principle, it is possible to take a short cut and go directly from the chemical energy of a fuel to electrical energy; in fact, this can actually be done, though there is as yet no practical and economical way of doing it on a large scale.

Let us now extend our chain in both directions to an end point. How did the chemical energy get locked up in the fuel in the first place? This came about through the transformation of radiant energy from the sun into chemical energy in a growing plant through a mechanism about which little is known at the present time. This process is also very inefficient as far as conversion of the total radiant energy falling on a given area of land to chemical energy in the plant is concerned; under favorable conditions the efficiency is about 3 per cent.[1] Heat and pressure, possibly aided by bacteria, have caused chemical reactions in the substance of the plant that finally changed it into coal, which from the energy point of view is simply fossilized sunlight.

To extend the other end of the chain, the chemical energy of the system in the storage battery can be reconverted to electrical energy and this, in turn, to radiant energy in an incandescent lamp. The proportion of the original chemical energy that finally gets into the desired form as light is very small, not over 2 per cent. Finally, the radiant energy is converted to heat energy at the temperature level of the surroundings, and in this form it is no longer available for further transformation.

This is the typical history of all energy transformation chains. The ultimate source of all terrestrial energy is the sun, and the ultimate destination is thermal energy in the matter on the earth's surface. Once the energy has reached this last stage, it is completely lost as far as further transformations are concerned because there is no longer any driving force available.

THE SECOND LAW OF THERMODYNAMICS

Limitations of the First Law.—Broadly speaking, there are two aspects of changes or processes with which we are mainly concerned in considering them from the thermodynamic point of view. (1) What energy change is associated with the process? (2) Will the change occur spontaneously and, if so, to what extent? Thus, in dealing with such things as heat balances, heats of reaction and of solution, and work of isothermal compression, we are concerned with questions that belong in class 1.

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[1] Of course, the chief reason for the low efficiency is the fact that only a relatively narrow portion of the spectrum of the sun's radiation is effective in photosynthesis.

When we consider chemical equilibrium, the work obtainable from heat, or that required for refrigeration, then we introduce questions that come under class 2.

Consider the case of the chemical reaction in a little more detail. If a reaction takes place from a given initial state of the reactants to a given final state of the products, all at a given temperature, how much heat is evolved and how is this amount changed as the pressure and temperature of the system change? These are questions of the first type. Will the reaction proceed spontaneously from the given initial to the final state? What is the equilibrium point at which no further change will occur, and how is this point affected by temperature and by pressure? If the reaction will not proceed spontaneously in the direction and to the extent desired, how much energy in the form of work must be applied to bring it about? These are questions of the second class. Now, the first law of thermodynamics is applied in answering questions of the first type; but this law is not, by itself, adequate to deal with questions of the second class, and another broad principle—the second law of thermodynamics—is invoked.

Various spontaneous, or irreversible, processes were considered in Chap. I. The first law deals with the amounts of energy in various forms that are involved in these processes, but it is not concerned with the direction of the change. There is nothing in the first law to deny the possibility that water will flow uphill or that heat will flow from a region of lower to a region of higher temperature or that gases will unmix. The second law does deal with just these things and is merely a way of stating our general experience with spontaneous processes or the tendency to change.

Reasons for Irreversibility.—It may be interesting to consider very briefly the underlying reasons why changes are irreversible. There is, of course, no loss of energy in the change, but the energy passes into an unavailable form that is not capable of performing work. As long as the energy is associated with a directed force or potential such as a fluid pressure or an e.m.f. or a temperature difference so that there can be an action in a definite direction, it is available for work; but as soon as any of the energy becomes converted to a form associated with the chaotic, or random, motion of molecules, it is then unavailable because the chances are so exceedingly small that these random motions can ever again become sufficiently oriented to yield a directed force.

This does not mean that ordinary heat energy, the energy associated with a transfer of heat, is always unavailable for transformation to work. When a transfer of heat is associated with a directive force such as a gas pressure or an e.m.f., the heat can then be partly transformed to work. Unlike a coiled spring or a raised weight or a compressed gas, it has no

directive force within itself, so that, whenever heat is generated by the action of a force, the action can never be reversed without calling on some outside agency for aid.

Briefly, it might be said that the fundamental reason for irreversibility is our inability to deal with individual atoms and molecules.

Let us illustrate some of these ideas by considering the concrete case of a waterfall. If 1 lb. of water falls freely through a height of 778 ft., the kinetic energy (neglecting any air friction) is converted at the base of the fall to 1 B.t.u. of thermal energy (first law) and this energy is entirely in the form of random, or undirected, motions of the molecules of the water. This amount of thermal energy is sufficient to raise the pound of water back to its original level, and there is nothing inconsistent with the first law in the idea that the thermal energy should be used to restore the water to its initial state, or, in other words, reverse the process. The only restriction imposed by the first law is that the water must cool 1°F. in the process. The difficulty is that the reversal requires a directed force, and the chances that the myriads of molecules with their random motions will ever happen to orient themselves in any given way so as to yield a directed force capable of delivering the necessary work is so extremely slight that it is for all practical purposes an impossibility. Strictly speaking, however, it is only an *improbability*, and this point of view is worth considering a little further because it gets at the very roots of the second law.

The case of solids may seem to be somewhat in conflict with this idea of a spontaneous process going from an ordered to a chaotic state. In the case of solids, the tendency is to change in the opposite direction, from the random state to the state of a perfect crystal, which represents perfect order. But in such a case the question of surface energy enters. A solid tends to go to a single crystal because that has the least surface energy.

Probability and the Second Law.—The second law is merely a statement of the impossibility of spontaneous, or irreversible, processes reversing themselves. The underlying reason for this irreversibility is the passage of a system from an "ordered," or directed, arrangement to a chaotic, or random, one. It is also the change from a highly improbable state to a much more probable one. To make this clearer, consider the simple analogy of a deck of cards, arranged in four hands of 13 cards each. There is a total of 635,000,000,000 different possible arrangements, or hands. The very orderly arrangement in which all 13 cards are of one suit is no more improbable than any other *one particular* arrangement that may be quite thoroughly shuffled; but there are only 4 of the all-one-suit arrangements possible, and there are about 1.37×10^{11} possible 4-4-3-2 arrangements. The chances, therefore, of getting 13 cards of one suit

from a well-shuffled deck as compared with a 4-4-3-2 hand are only 1 to 3.4×10^{10}. To go from shuffled cards to shuffled molecules, the principle is still the same, and because the numbers are so very much greater the chances of an orderly arrangement arising from a random mixture are infinitesimal.

Thus, suppose we have two vessels connected by a pipe. In one we place nitrogen gas and in the other oxygen and then allow the two to mix. In a relatively short time we have a completely random mixture as far as any analysis would show. Owing to the continued motion of the molecules the shuffling goes on forever, but the chances of a reproduction of the original configuration are so exceedingly small that we can dismiss it entirely from consideration and say that the process is completely irreversible.

The point that a process is irreversible because of the *improbability* rather than the *impossibility* of an unshuffling of a chaotic system is only of philosophic interest, but before leaving the subject it may be worth while to mention an ingenious mathematical demonstration of this given by Lotka.[1] A system of 26 vibrating pendulums, each with a different period, is set in motion at a given instant. Soon the system seems to be a random one as far as distribution of the pendulums on given sides of a center line is concerned. Actually, however, the system has a definite period, which can be calculated; and an observer who could wait 7,385 years would find that at a particular instant a complete unshuffling occurred and the initial configuration was reproduced.

Maxwell was one of the first to perceive that the reason for irreversibility is our inability to deal with individual molecules. He imagined a being, known commonly as "Maxwell's demon," who was small enough to deal with individual molecules and who could therefore readily violate the second law. If such a demon controlled the opening and closing of a very small aperture between two vessels containing gas at a uniform temperature, he could cause a temperature difference to develop by unshuffling the "hot" and "cold" molecules through proper manipulation of the shutter, or he could separate a mixture of two gases. Certain bacteria are able to assume a role approaching that of Maxwell's demon when they bring about the separation of racemic mixtures.

Statements of the Second Law.—Any statement of the second law is merely a denial of the possibility of a spontaneous process reversing itself. Clausius in 1851 gave the following statement: "It is impossible for a self-acting machine, unaided by any external agency to convey heat from one body to another at a higher temperature." This would appear at first sight to be a statement of rather limited scope since it deals only with

[1] LOTKA, A. J., "Elements of Physical Biology," The Williams & Wilkins Company, Baltimore, 1925.

a particular irreversible process, *viz.*, a transfer of heat.   As a matter of fact, it is perfectly general.   As is evident from the previous discussion, all irreversible processes are fundamentally the same and, if any one of them can be reversed, all the others can.   No proof of this will be attempted, but one example may be cited to illustrate it.

Suppose that a gas has expanded isothermally from a reservoir at given pressure to another at lower pressure without the performance of any external work.   This is clearly an irreversible process.   It can be reversed, but only by getting aid from an external mechanism, and then some other system would be run down.   Suppose, however, that we have a heat reservoir at the same temperature as the gas.   If we do *not* deny the possibility of heat being conveyed from one body to another at higher temperature without external aid, then we can imagine that there is some kind of mechanism which will allow a temperature difference to be developed in the heat reservoir.   As a result of this temperature difference, some of the heat in the reservoir can be used to obtain work by means of a heat engine, and this work can then be applied to restoring the expanded gas to its initial pressure by compressing it isothermally. The work of compression appears as heat that is returned to the reservoir. The net result is the reversal of the "irreversible" gas expansion *without leaving any changes elsewhere.*   If, however, we deny, with Clausius, the heat transfer from lower to higher temperature, then the whole scheme fails and the gas expansion is irreversible.   Because of the fact that any two irreversible processes can be linked in this way, a denial of the possibility of reversing any one will automatically include all the others, and so Clausius' statement is a perfectly general one.

Lord Kelvin stated it independently as follows: "It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of surrounding objects."   Objections have been raised to this statement.   Thus, if gas at atmospheric temperature is confined under pressure in a thermally insulated cylinder and allowed to expand against an external force, work will be done and the gas will cool far below the temperature of the surroundings.   Such a process, however, will not continue to deliver work; any attempt to make it continuous means that the gas must be restored to its initial condition (*i.e.*, the process must be cyclic), and this will require the expenditure of an amount of work at least equal to that gained from the expansion.

Planck has given a statement that is an improvement over that of Kelvin: "It is impossible to construct a machine which will operate in a cycle and produce no effects but the raising of a weight and the cooling of a heat reservoir."   This merely means that the energy contained in a given heat reservoir cannot be tapped to produce a useful effect unless

there is another reservoir available at a lower temperature. If this were possible, any ocean vessel, any train, or any automobile could be propelled without fuel, for the surrounding water or atmosphere would supply an almost inexhaustible amount of energy. Such a possibility is sometimes referred to as "perpetual motion of the second kind," and Kelvin's or Planck's statement is said to deny this kind of perpetual motion. Either of these statements can be closely linked to that of Clausius; for it should be obvious that, if work can be continuously obtained from a heat reservoir, then heat can be conveyed from a lower to a higher temperature without calling on any external agency. Likewise, it is clear that any irreversible process can be reversed without the necessity of leaving changes in some other system.

Many special statements of the second law can be made with reference to particular phenomena. One of the most important of these has to do with the amount of work that can be obtained from a given quantity of heat transferred to the working substance of a heat engine. This leads us to a consideration of a principle of great practical importance and of considerable interest from a historical viewpoint.

Carnot's Principle.—This famous principle, enunciated by Carnot in 1824, formed the basis for the subsequent development of the second law and is the foundation on which all heat-engine theory is built. It may be stated thus: The maximum possible efficiency of any heat engine working between two temperature levels is a function of these two temperatures only and is in no way dependent on the mechanism or the working substance. The working substance is simply the fluid, such as air, steam, or ammonia, that goes through the cycle of changes in the engine. The efficiency of a heat engine is defined as the work delivered divided by the heat taken in. The simplest imaginable heat-engine cycle is one in which all heat is taken into the engine from one reservoir at constant temperature t_1 and all heat is rejected to a single reservoir maintained at a constant lower temperature t_2. The reversible execution of such a cycle was described in detail in Chap. I. It is commonly known as the "Carnot cycle" because Carnot deduced his principle from a consideration of such a cycle. It is mainly of historical interest at the present time. For the analysis of the performance of heat engines, refrigerating systems, compressors, etc., other ideal cycles are used, more closely approximating the actual ones than the Carnot cycle. It is still of value for preliminary analysis and as an introduction to the more complex cycles. Because it is simple, the reasoning based on it is clearer and not obscured by complications of a practical character.

Proof of the Carnot Principle.—Carnot's proof of this theorem was based on the old caloric theory of heat, which was completely overthrown by the work of Joule. Clausius and Kelvin, working independently,

realized that Carnot's proof was no longer valid but that his principle was in accord with experience and was undoubtedly correct. Both gave new proofs, which were consistent with the newer conception of heat as a form of energy. The axioms that they stated as the basis for the proof are the statements of the second law that have already been cited. A brief form of Kelvin's proof of the Carnot principle will now be given.

In Fig. II.1, let there be two heat reservoirs at the constant temperatures t_1 and t_2. These temperatures can be measured on any scale whatever; for the present purpose, it is necessary only that they be constant and differ from one another. Let t_1 be greater than t_2. Consider a heat
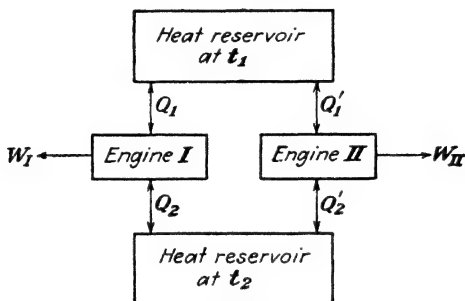
FIG. II.1.—Illustrating one proof of the Carnot principle.

engine, I, which operates on the simplest possible cycle, *viz.*, the Carnot cycle, between these two temperatures. Assume that it takes in the quantity of heat Q_1 from the reservoir at t_1 and rejects Q_2 to the reservoir at t_2. Our discussion in the previous chapter of the operation of this cycle showed that a rejection of heat at the lower temperature was necessary. We need make no restriction concerning the exact nature of the mechanism or the working substance used in the engine. Now, by the first law, the work done W_I will equal $Q_1 - Q_2$. If the engine is operated in the ideal, reversible manner previously discussed (which implies many things not capable of practical attainment, such as frictionless pistons, thermally nonconducting materials, and similar thermodynamic paraphernalia that are necessary to avoid irreversible effects), this work will be the maximum attainable with the particular cycle and working substance chosen. Now consider another engine, II, working on any cycle you please and using any working substance whatever but taking in heat Q_1' at t_1 and rejecting heat Q_2' at t_2. Choose the amount of working substance so that Q_1 will equal Q_1'. Now suppose that engine II is more efficient than engine I so that when operated as a work producer it delivers more work than I with the same heat intake. Expressing this by an equation,

$$W_{II} = W_I + \Delta \qquad (II.3)$$

and since $W_{II} = Q_1' - Q_2'$ and $W_I = Q_1 - Q_2$ by the first law, then

$$Q_1' - Q_2' = Q_1 - Q_2 + \Delta \tag{II.4}$$

Now, since engine I is reversible, it can be run in the reverse direction and when supplied with the work W_I will pump heat Q_2 from the reservoir at t_2 and deliver Q_1 to the reservoir at t_1. Let engine II operating as a heat engine drive engine I operating as a heat pump. Since $Q_1 = Q_1'$, then

$$Q_2 = Q_2' + \Delta \tag{II.5}$$

The result of this combination is that we gain a net amount of work Δ, and this is accompanied by the abstraction of an equivalent amount of heat from the reservoir at t_2. There is nothing contrary to the first law in this. It is contrary to experience, however, and Kelvin's or, better, Planck's statement of the second law specifically denies the possibility of doing just this thing. Therefore, if we accept the axiom, engine II cannot be more efficient than I, nor can any other engine working between the same temperature limits.

Likewise, no engine can be less efficient than I and still be reversible, as the following reasoning will show. Suppose engine II were reversible but less efficient than I. Let I drive II as a heat pump, and let

$$W_I = W_{II} \tag{II.6}$$
$$\therefore Q_1 - Q_2 = Q_1' - Q_2' \tag{II.7}$$

But if the efficiency of II is less than that of I,

$$\frac{Q_1' - Q_2'}{Q_1'} < \frac{Q_1 - Q_2}{Q_1} \tag{II.8}$$

Combining with Eq. (II.7), it is evident that

$$Q_1' > Q_1 \tag{II.9}$$

and also

$$Q_2' > Q_2 \tag{II.10}$$

That is, the net result of the combination of engines (self-acting machine) is a flow of heat from the body at t_2 to that at t_1. This is specifically declared impossible by Clausius' axiom.

The conclusion is that all reversible engines operating between given temperature levels have the same efficiency, that this efficiency is a maximum, and that it depends only on the temperatures.

This proof is so general and abstract in character that it fails to satisfy many who are accustomed to thinking in more concrete terms. To others it may seem like such an obvious conclusion that proof is not required. As a matter of fact, proof of the principle in any such formal fashion is no longer necessary; for an enormous structure of experimental fact and

experience has been built upon it, and not a single fact has yet been definitely demonstrated to be contrary to it.   The proof is, nevertheless, of the greatest interest because of the very fact that the principle that is proved in such a simple manner has been found to be of such universal validity and to underlie so many fields of science and engineering. Although the principle is absurdly simple in statement, its full implication is not readily grasped and it requires a long experience in applying it to a variety of problems before one begins to have an appreciation of its amazing versatility.

It should be continually kept in mind that all our reasoning about the conversion of heat to work is concerned with cycles.   The reasoning does not hold for parts of a cycle but only for the whole.   Thus, in the isothermal expansion of a gas, substantially all the heat taken in is converted to work; and if this is followed by an adiabatic expansion, we end up with considerably more work done than corresponds to the heat taken in.   The compensation occurs in returning the working fluid to its initial state.   This requires that work be done; and when the cycle is completed, then the net work gained is much less than the equivalent of the heat taken in.

CHAPTER III

QUANTITATIVE DEVELOPMENT OF THE TWO FUNDAMENTAL LAWS. THE THERMODYNAMIC FUNCTIONS

In the previous chapter the ideas and facts that form the basis of the two fundamental laws of thermodynamics were presented and developed in a qualitative way. In order to apply these principles to actual numerical problems they must be given a more exact, quantitative expression. This is most conveniently done by means of certain functions or properties that have been defined and are in common use. Unfortunately, some confusion arises from the fact that the symbols used to represent these functions have not been standardized. We shall endeavor to adhere to the system of nomenclature most commonly used by American writers in the field of chemical thermodynamics.

The treatment in this chapter will refer primarily to simple static, or nonflow, systems consisting only of a single phase and a single component or a mixture of constant composition. The general principles involved are, of course, applicable to more complex systems. However, it seems desirable to illustrate the principles first by the simpler cases and then proceed later to generalize.

THE COMMON THERMODYNAMIC FUNCTIONS

The functions may conveniently be divided into two groups, (1) those which involve only the first law and (2) those which involve both laws but which are particularly associated with the second law. The first of those of class 1 is the energy content, E, which has already been discussed at some length. The other function of class 1 is the enthalpy H or "heat content" as it is sometimes called. This must not be confused with quantity of heat transferred, which is represented by the symbol Q. H is a definite property of a system, whereas Q is not. To lessen the possibility of confusion most writers now prefer the name "enthalpy" for H instead of the older term "heat content," and we shall adopt this practice.

The second-law functions are thermodynamic, or absolute, temperature T, the entropy S, the work function A (also called "maximum work" though it may actually be minimum work that is in question), and the free energy F. Absolute temperature was first defined by Lord Kelvin in 1848, and entropy was introduced by Clausius in 1851. The function A was originally called "free energy" by Helmholtz, and it is

still called that by most European writers.   The F function was first defined and used by Willard Gibbs in 1875, though some years earlier Massieu had defined a related function.   It was called by Gibbs "thermodynamic potential" and represented by the symbol ζ.   The use of the term "free energy" for this function was started by G. N. Lewis and has since become universal practice in this country.   There are certain other functions, of a somewhat less fundamental character, that have proved useful in the treatment of solutions; reference to them will be made later.

All the functions mentioned, with the exception of thermodynamic temperature, are extensive properties, *i.e.*, depend on the mass of the system.   It will be generally understood that the symbol for each function refers either to a unit mass or to a molal mass, usually the latter.   When it is necessary to represent the total value of one of these properties for the system as a whole, the same symbol will be used, but in boldface type.

The remainder of this chapter is devoted to the development of the relationships between these functions and the common variables of state that are needed for numerical calculations.

THE ENERGY CONTENT

It was shown in the previous chapter that the definition of an energy content, which is a definite property of any system, is the essence of the first law of thermodynamics.   Equation (II.2) may now be written in differential form as follows:

$$dE = dQ - dW \qquad\qquad (III.1)$$

dE is a perfect differential since it is the derivative of a point function, but dQ and dW merely represent infinitesimal quantities of heat and work and are not derivatives of any functions.   This means that, if a finite change from state 1 to state 2 is under consideration, we may write

$$\int_1^2 dE = E_2 - E_1 = \int_1^2 (dQ - dW) \qquad\qquad (III.2)$$

In other words, dE can be integrated at once without regard to the nature of the change because E is a property and its value depends only on the initial and final states and in no way on the particular path of the change. The second integration, however, cannot be performed until we know something about the exact way in which the change occurred and so can express dQ and dW in terms of certain properties.   In other words, both Q and W depend on the path taken and are not determined by the initial and final states.

We shall deal only with differences in E since nothing is known about the absolute value of this function.   For convenience, E may be taken as equal to zero at some arbitrary standard state, but the more usual procedure is to make $H = 0$ at a reference state and determine E from it.

In accordance with Eq. (I.19), we may write

$$\frac{\partial^2 E}{\partial x\,\partial y} = \frac{\partial^2 E}{\partial y\,\partial x} \qquad \text{(III.3)}$$

where x and y are any two independent variables defining the state of the system.   This equation and similar ones for other functions are useful in certain derivations, as we shall show later.

Certain special forms of Eq. (III.1) will be found useful in the subsequent treatment.   For example, if the only force acting on the system is a fluid pressure, Eq. (III.1) can be written[1]

$$dE = dQ - p\,dv \qquad \text{(III.4)}$$

If in addition, the change occurs at constant volume, then

$$dE = dQ = C_V\,dt \qquad \text{(III.5)}$$

where C_V is the specific heat at constant volume.

Energy content is an extensive property; that is, it is strictly proportional to the mass of the system.   Furthermore, the energy contents of any portions of matter regardless of state or composition are additive; but it should be noted that if two systems are mixed there may be interaction with the surroundings, resulting in an energy change, so that the energy content of the mixture is not the sum of the energy contents of the components, except in a case where the systems are isolated from the surroundings.

ENTHALPY

Definition.—This is a compound function formed from other more simple ones and is defined in integral form by the equation[2]

$$H = E + pv \qquad \text{(III.6)}$$

It has been defined because in many applications the summation of E, the energy content, and pv, pressure-volume product, constantly occurs and it is a convenience to treat this sum as an entity.   Although, in

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[1] It is important to note that the use of the equation

$$dW = p\,dv$$

where p refers to the pressure of the system itself, implies a reversible process.   If any degree of irreversibility exists, one should write

$$dW < p\,dv$$

[2] Note that E and pv must be expressed in the same units before the addition can be made.

general, it is not to be identified with Q, a quantity of heat transferred, in certain special cases it does become identical with Q, and therein lies one of the chief reasons for its existence.   From its definition it is obviously a property, and hence changes in its value are determined solely by initial and final states.

In certain changes, such as the isothermal expansion of an ideal gas, there will be considerable heat Q transferred but no change in H.   Again, in the adiabatic throttling expansion of a nonideal gas, both Q and ΔH are zero.   In the reversible adiabatic expansion of a gas, Q is zero but H decreases.   These statements are made to emphasize again the fact that heat Q and enthalpy H are two quite different things.

Like E, H is an extensive property and obviously has no known absolute value.   We shall deal only with differences in enthalpy ΔH, and for convenience an arbitrary value will be assigned for some standard state.

Constant-pressure Process.—By differentiation of Eq. (III.6),

$$dH = dE + p\,dv + v\,dp \qquad \text{(III.7)}$$

For a *constant-pressure* process this reduces to

$$dH = dE + p\,dv \qquad \text{(III.8)}$$

By comparison with Eq. (III.4) and from the definition of C_p it is clear that

$$dH = dQ = C_p\,dt \qquad \text{(III.9)}$$

for any constant-pressure change in which the pressure is the only force acting.   Putting Eq. (III.9) in integral form,

$$\Delta H = Q = \int_{t_1}^{t_2} C_p\,dt \qquad \text{(III.10)}$$

This is an exceedingly important equation from the standpoint of practical application.   Stated in words, a change in function H is a measure of heat effects at *constant pressure*.   Many processes of industrial importance occur at constant pressure, and to obtain a value for the heat evolved or absorbed in such a process it is necessary only to subtract the values of H for the two terminal points of the process.   This is the fundamental basis for all total heat charts or tables and makes the calculation of heat effects very simple for all systems for which the values of H have been plotted or tabulated.

Illustration 1.—How much heat must be added to 1 lb. of water at 327.8°F. and 100 lb. per sq. in. absolute pressure to change it to superheated steam at 500°F. and the same pressure?

From the Keenan-Keyes tables[1] we find that

H for superheated steam at 500°F. and 100 lb. per sq. in. pressure = 1,279.1 B.t.u. per
lb. (page 50)
   H for water at 327.8°F. and 100 lb. per sq. in. = 298.4 B.t.u. per lb. (page 36)
      ∴ *Q* = Δ*H* = 1,279.1 − 298.4 = 980.7 B.t.u. per lb.

It must be emphasized that this simple relationship holds only for those changes which occur at *constant pressure*. It should not be inferred from this, however, that the function *H* is useful only for a constant-pressure change. Later we shall have occasion to apply it to an important type of process that is far from being at constant pressure.

Relation of Δ*H* and Δ*E*.—From Eq. (III.5) it should be clear that heat effects at *constant volume* are a measure of changes in energy or, conversely, heat evolved or absorbed in constant-volume processes is obtained from differences in *E* just as the heat effect at constant pressure is obtained from differences in *H*. If we know the pressures and volumes at the terminal points of the change, we can readily obtain Δ*E* from Δ*H*, or vice versa, through the equation

$$\Delta H = \Delta E + \Delta(pv) \tag{III.11}$$

For example, take the case of vaporization of a fluid. If the liquid were evaporated at constant pressure in a calorimeter, the heat required would be a measure of Δ*H* or the difference between the heat content of the vapor and that of the liquid. Δ*E* could then be calculated from Eq. (III.11) if the specific volumes of both vapor and liquid were known. In all cases where the substance is in a condensed state (*i.e.*, liquid or solid) at both terminal points, it is clear that the term Δ(*pv*) will be small and the difference between Δ*H* and Δ*E* will be small and in many cases entirely negligible.

√ **Illustration 2.**—Liquid pentane at its boiling point, 172.1°F., under a pressure of 50 lb. per sq. in. abs. has a specific volume of 0.02836 cu. ft. per lb. and an enthalpy of 76.64 B.t.u. per lb. The saturated vapor at the same pressure has a volume of 1.672 cu. ft. per lb. and an *H* of 213.1. What is the change in energy accompanying the vaporization process?

By Eq. (III.11), Δ*E* = Δ*H* − Δ(*pv*)
   Δ*H* = 213.1 − 76.6 = 136.5 B.t.u.
   Δ(*pv*) = $p_2 v_2 - p_1 v_1 = p(v_2 - v_1)$ = 50 × 144(1.672 − 0.028)
      = 11,850 ft.-lb.

   11,850 ft.-lb. = $\dfrac{11,850}{778}$ B.t.u. = 15.2

   ∴ Δ*E* = 136.5 − 15.2 = 121.3 B.t.u.
      = 121.3 × 778 = 945,000 ft.-lb.

[1] KEENAN, J. H., and F. G. KEYES, "Thermodynamic Properties of Steam," John Wiley & Sons, Inc., New York, 1936.

ABSOLUTE, OR THERMODYNAMIC, TEMPERATURE

Fundamental Basis.—The desirability of an absolute scale of temperature, independent of the properties of any particular substance, was pointed out in Chap. I.   A temperature scale based on the ideal gas is, in a sense, an absolute scale, but it is a purely imaginary or hypothetical one in that the ideal gas has no practical reality.   There is no ideal gas; but, of course, many gases are close approximations to it in certain regions of temperature and pressure.   At very low temperatures there is no substance that will even approximately represent the behavior assumed for an ideal gas.

Fig. III.1.—Diagram illustrating the definition of absolute temperature.

Lord Kelvin, in 1848, recognized that the Carnot principle provided a sound basis for the definition of an absolute scale of temperature because it states that a certain quantity, *viz.*, the efficiency of a heat engine, is a function only of certain temperatures and is *entirely independent of the working substance* used.   In other words, a Carnot heat engine, broadly speaking, can be used as a thermometer, and it will always register the same readings at a given set of temperatures, regardless of whether it is filled with mercury or alcohol or a gas or any other substance.

Definition of a Function T.—Carnot's principle is stated mathematically as follows:

$$\text{Efficiency} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = \phi(t_1,\, t_2) \qquad \text{(III.12)}$$

where Q_1 = quantity of heat taken in by the reversible heat engine from the constant-temperature heat reservoir at t_1.

Q_2 = heat rejected to the reservoir at t_2.

ϕ = some unknown function of the two temperatures that depends on how the scale of temperatures is defined.

Since $(Q_1 - Q_2)/Q_1 = 1 - (Q_2/Q_1)$, we may also write

$$\frac{Q_1}{Q_2} = \phi(t_1, t_2) \qquad \text{(III.13)}$$

Referring to Fig. III.1, assume that there are constant-temperature heat reservoirs at the three temperatures t_1, t_2, and t_3 and three heat engines operating on Carnot cycles with a given working substance as follows:

Engine I takes in heat Q_1 at t_1 and rejects heat Q_2 at t_2.

Engine II takes in Q_2 (the heat rejected by I) and rejects Q_3 at t_3.

Engine III takes in Q_1 at t_1 and rejects heat at t_3.

Now since all reversible engines operating between the same temperature limits have the same efficiency, engines I and II taken together have the same efficiency as III and therefore must reject the same quantity of heat at t_3, *viz.*, Q_3.   If this were not so, the second law would be violated.

For the three engines we can write expressions analogous to Eq. (III.13),

$$\frac{Q_1}{Q_2} = \phi_1(t_1, t_2) \qquad \text{(III.14)}$$

$$\frac{Q_2}{Q_3} = \phi_2(t_2, t_3) \qquad \text{(III.15)}$$

$$\frac{Q_1}{Q_3} = \phi_3(t_1, t_3) \qquad \text{(III.16)}$$

Dividing Eq. (III.16) by Eq. (III.15) and comparing with Eq. (III.14),

$$\frac{Q_1}{Q_2} = \frac{\phi_3(t_1, t_3)}{\phi_2(t_2, t_3)} = \phi_1(t_1, t_2) \qquad \text{(III.17)}$$

This can be true only if

$$\phi_1(t_1, t_2) = \frac{\psi_1(t_1)}{\psi_2(t_2)} \qquad \text{(III.18)}$$

with similar expressions for the other two functions.   The exact form of the functions is unknown and will depend on the way in which the temperature scale was defined.   Let us now define a new scale of temperatures by the equation

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \qquad \text{(III.19)}$$

where $T_1 = \psi_1(t_1)$ and $T_2 = \psi_2(t_2)$.   This defines a scale of temperatures such that the ratio of any two temperatures on it equals the ratio of heats taken in and rejected by a reversible heat engine operating between these two temperatures.   The choice of this particular form of the function, as Lord Kelvin noted, is arbitrary.   He might have chosen $e^{T}*$ or $\log_{10} T$ or any other form; but the reason for the particular choice he made is the very obvious one that it gives a scale which is identical with the ideal-gas scale, and therefore actual gases will give a good approximation to it in most cases.

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* As a matter of fact, the absolute scale originally proposed by Kelvin was based on a function of this form, but it never came into general use.   It has certain advantages over the common Kelvin scale when operating in the region close to absolute zero on the common scale.

For proof of the identity of the Kelvin thermodynamic scale and the ideal-gas scale, it is necessary merely to operate a Carnot cycle using an ideal gas as working fluid. Temperature θ on the ideal-gas scale is defined by the relation

$$pv = R\theta$$

and it is readily shown that

$$\frac{Q_1}{Q_2} = \frac{\theta_1}{\theta_2}$$

where Q_1 and Q_2 are heats taken in and rejected, respectively, by a Carnot engine operating with an ideal gas between reservoirs whose temperatures are θ_1 and θ_2 on the ideal-gas scale.

Temperature Intervals.—From Eq. (III.19), for engine I,

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \tag{III.20}$$

If another engine (engine II in Fig. III.1) takes in Q_2 (the heat rejected by the first engine) and rejects Q_3 to another reservoir at T_3, then we have

$$\frac{Q_2 - Q_3}{Q_2} = \frac{T_2 - T_3}{T_2} \tag{III.21}$$

Dividing Eq. (III.21) by Eq. (III.20) and noting that $Q_2/Q_1 = T_2/T_1$, we get

$$\frac{Q_1 - Q_2}{Q_2 - Q_3} = \frac{T_1 - T_2}{T_2 - T_3} = \frac{W_I}{W_{II}} \tag{III.22}$$

Stated in words, any two intervals on this absolute scale have the same ratio as the amounts of work done by reversible engines operating between the respective temperature limits.

The length of a degree is entirely arbitrary. If we imagine 100 Carnot engines, the first one taking in heat from a reservoir maintained at the normal boiling point of water and the last one rejecting heat to a reservoir maintained at the ice point and each one taking in the heat rejected by the preceding one operating at the higher temperature level, and if these engines all do the same amount of work, then by Eq. (III.22) we define 100 equal temperature intervals between the two terminal points. Each interval represents a degree on the Kelvin or centigrade absolute scale. Similarly, we can define 180 equal intervals between these same two points, and each of these represents a degree Rankine or Fahrenheit absolute.

Absolute Zero.—Since $Q_1T_2 = Q_2T_1$, it is clear that $T_2 = 0$ if $Q_2 = 0$. This means that zero on the absolute scale is the temperature of the heat reservoir to which a reversible heat engine rejects no heat, all the heat

taken in having been completely transformed to work.[1]   This gives a real physical meaning to the concept of absolute zero that it did not possess as long as it was defined purely on the basis of the behavior of an ideal gas.   From the second law of thermodynamics and the change of certain properties with temperature, it is possible to locate the absolute zero as somewhere between 273.1 and 273.2°C. below the ice point.   Its value is fixed by measurements that are made at temperatures far removed from absolute zero.   For example, if a gas is expanded isothermally one can measure values of the ratio pv/p_1v_1; and if these values are plotted vs. p and extrapolated to $p = 0$, we get the value of p_0v_0/p_1v_1.   Let this value for a given gas at t_1 be λ_1.   Let the corresponding value for t_2 and the same initial value p_1v_1 be λ_2.   Since the products p_0v_0 are limiting values for $p = 0$ where the gas is ideal, then

$$\frac{\lambda_2}{\lambda_1} = \frac{\theta_2}{\theta_1} = \frac{T_2}{T_1}$$

Measurements on a number of gases at $t_1 = 0°C.$ and $t_2 = 100°C.$ give an average value of 1.36607 for this ratio.   From

$$\frac{T_2}{T_1} = 1.36607$$

and

$$T_2 - T_1 = 100$$

we get

$$T_1 \ (t = 0 \text{ on centigrade scale}) = 273.16°K.$$

The exact value is still a matter of dispute.   We shall arbitrarily choose the value $-273.2°C.$ or $-459.7°F.$ For almost all engineering work these can be rounded to $-273°C.$ and $-460°F.$, respectively.

It is of interest to note that recently there has been considerable activity in scientific circles directed toward the production and utilization of temperatures below $1°K.$ These low temperatures are of especial interest in connection with the third law of thermodynamics.   Temperatures as low as $1.5°K.$ can be produced by methods similar in principle to those used in ordinary refrigeration practice, with helium as the working substance.   Below $1.5°K.$ an entirely different method is used —adiabatic demagnetization—first proposed by Giauque.[2]   In this way, temperatures as low as $0.005°K.$ have been produced.   For further details on the theory and technique of this interesting method, a review paper by Giauque[3] is recommended.

[1] Conversion of more than 100 per cent of the heat to work would, of course, constitute a violation of the first law.

[2] W. F. GIAUQUE, *J. Am. Chem. Soc.*, **49**, 1864 (1927).

[3] W. F. GIAUQUE, *Ind. Eng. Chem.*, **28**, 743–750 (1936).

Relation of Absolute Scale to Scales Based on Properties.—The relative simplicity of the form of the equations of thermodynamics is due to the way in which the absolute temperature was defined by Kelvin. If a temperature scale based on the properties of some particular substance were used, all these equations would be far more complex. In all ordinary thermodynamic formulas, the temperature implied is always the absolute, or thermodynamic, temperature and no other. In a sense, any thermodynamic formula or equation may be regarded as defining absolute temperature. This does not mean that thermodynamic formulas are purely matters of definition without real basis of fact, because the very fact that an absolute temperature can be defined is the heart of the second law and from this law many exact relationships have been derived, no one of which has yet been found to be contrary to experience.

Temperatures must be measured on the basis of the change of some property with the temperature, and then these temperatures must be corrected in some way to place them on the Kelvin scale. Thus it is required to evaluate the function in the equation

$$T = \phi(t) \qquad \text{(III.23)}$$

This can be done through the use of any of the common thermodynamic equations relating T to other properties. For further details on this subject consult the references given below.[1]

THE ENTROPY FUNCTION

General Statement.—This function was introduced by the German physicist Clausius in 1851. Owing to its abstract character it has always been a shibboleth for beginners in the study of thermodynamics, and many volumes have been written in an attempt to explain its physical significance and give it more of a semblance of reality. For the present, it will be regarded primarily as a mathematical function that offers the simplest means of making quantitative application of the second law. It will first be treated entirely from this viewpoint following the classical derivation of Clausius. The later work of Boltzmann, Planck, G. N. Lewis, and others has revealed the relationship of entropy to probability and has given it a greater physical significance. This will be discussed very briefly; but it is the author's belief that, for the purposes of applied thermodynamics, it is sufficient to regard entropy as a convenient mathematical function, and its physical interpretation will not be stressed. The engineer who is primarily interested in the transformation of heat into useful work may find it convenient to regard entropy as a

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[1] BUCKINGHAM, EDGAR, *Bur. Standards Sci. Paper* 57 (1907). ZEMANSKY, M. W., "Heat and Thermodynamics," 2d ed., McGraw-Hill Book Inc., New York, 1943.

measure of that portion of the heat energy transferred which is *unavailable* for work. This viewpoint will also be presented.

It was brought out in the previous chapter that the second law is merely a generalized statement of our experience with spontaneous processes or of tendency for change. To make the statement quantitative, there is required some function that always changes in a certain way during a spontaneous, or irreversible, process and therefore will characterize such a change. The function E has been defined to give quantitative significance to the first law, and it is the fundamental first-law function, H being merely a convenient function derived from it. E does not change in any characteristic way in a spontaneous process, and so it is of no fundamental value in the development of the second law. The
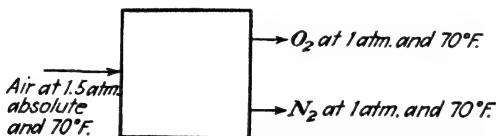
Fig. III.2.—A thermodynamically impossible process.

function that *is* fundamental to the development of the second law is entropy (combined, of course, with the concept of absolute temperature, upon which the definition of entropy depends), and one of the most satisfactory ways to think of it is merely as a mathematical quantity that greatly simplifies the quantitative development and application of the second law.

Let us briefly illustrate these ideas in a more concrete way. Figure III.2 represents the over-all result of an imaginary process for gas separation. As far as the thermodynamic possibility of the process is concerned, we need not consider what occurs inside the box, but we must show all material and energy exchanges between the box and its surroundings. Assuming that the gases are ideal, the proposed process involves no change in the energy content E, and there is no reason from the standpoint of the first law why the process is not a possible one. With the aid of the entropy function, however, it can readily be shown that the imagined process is an impossible one because it would involve a net decrease in entropy with no corresponding increase in the entropy of the surroundings.

Quantitative Definition.—We have already seen that the fundamental principle of Carnot combined with Kelvin's definition of an absolute temperature led to the simple equation

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \tag{III.24}$$

or
$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \tag{III.25}$$

Regarding the heat taken in from the source, Q_1, as positive and heat rejected Q_2 as negative, we may rewrite Eq. (III.25) as follows:

$$\sum \frac{Q}{T} = 0 \tag{III.26}$$

These relationships are only for the very simple Carnot reversible cycle in which all heat is taken into an engine at one temperature and all heat is rejected at some one lower temperature, both temperatures being constant throughout the process.   This is a simplified case which will seldom be
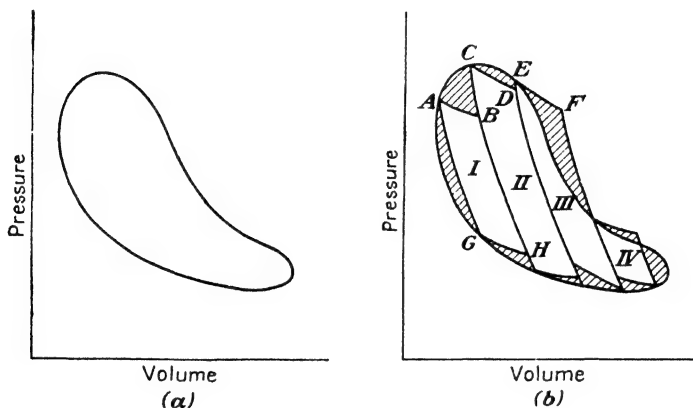
Fig. III.3.—Illustrating the definition of entropy.

met in practice, and it is desirable to generalize this result to apply to a more complex cycle where the temperatures at which heat is taken in and at which it is rejected are both changing continuously.

Consider any reversible cycle of changes through which the working substance of a heat engine may pass.   The conditions for reversibility have already been discussed and need not be repeated here.   Let the state of the working substance that goes through the cycle of changes be defined by two independent variables and represented on a *pv* plane as in Fig. III.3*a*.   Now let the cycle of Fig. III.3*a* be broken up into four simple Carnot cycles of two adiabatic lines and two isothermals each, as shown in Fig. III.3*b*.   The area of the four simple cycles will only approximate that of the original cycle, the differences (some plus and some minus) being indicated by the crosshatched areas.   A reversible engine operating on cycle I (*ABGH*) takes in heat Q_I at T_I (along isotherm *AB*) and rejects Q_I' at T_I' (along *GH*).   Similarly, an engine operating on cycle II takes

in Q_{II} at T_{II}, rejects Q'_{II} at T'_{II}, etc., for the other cycles. For each of these cycles we may write an equation similar to Eq. (III.25):

$$\frac{Q_I}{T_I} - \frac{Q'_I}{T'_I} = 0 \tag{III.27}$$

$$\frac{Q_{II}}{T_{II}} - \frac{Q'_{II}}{T'_{II}} = 0 \tag{III.28}$$

$$\text{Etc.}$$

Now, an engine operating on the stepwise cycle $ABCDEF$ . . . does work represented by the sum of the four areas enclosed by the isothermal and adiabatic lines since cycle work is equal to the enclosed area on a pv diagram. Furthermore, since it uses the same isotherms as the individual engines, the heat taken in and that rejected by this engine must be the algebraic summation of the corresponding heats of the individual engines. An engine working on the stepwise cycle may thus be taken as equivalent to the four separate engines, and we may write for it

$$\frac{Q_I}{T_I} + \frac{Q_{II}}{T_{II}} + \cdots - \frac{Q'_I}{T'_I} - \frac{Q'_{II}}{T'_{II}} - \cdots = 0 \tag{III.29}$$

This may be abbreviated simply to

$$\sum \frac{Q}{T} = 0 \tag{III.30}$$

the summation extending over the whole stepwise cycle. By taking the adiabatic lines closer together and utilizing more steps, it is clear that the same relation still holds and that the crosshatched area will become smaller. Now proceed to the limit and take the adiabatics so close together that the isothermals differ only by an amount dT, and the stepwise process becomes identical with the cycle of Fig. III.3a, the crosshatched area having been made vanishingly small. From the well-known methods of calculus, at the limit

$$\sum \frac{Q}{T} = \int \frac{dQ}{T} = 0 \tag{III.31}$$

From the standpoint of applied thermodynamics this is an exceedingly important equation. Stated in words, it says that for any cycle involving heat and work effects, however complex but always executed in a *completely reversible manner*, the algebraic sum of all heat effects divided by the respective absolute temperatures at which the transfers occur is equal to zero. From the discussion of functions and properties in Chap. I, it should be clear that dQ/T is like the derivative of a property, or is a perfect differential. In a cycle of changes the total change of the quantity whose infinitesimal value is dQ/T is zero, and this simply means that the

quantity has a definite value characteristic of a given state and it is therefore a property. This property whose derivative is dQ/T was given the name "entropy" by Clausius and will be represented by the letter S. Thus we write

$$dS = \frac{dQ}{T} \qquad \text{(III.32)}$$

and

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dQ}{T} \qquad \text{(III.33)}$$

Equations (III.32) and (III.33) may be regarded as the quantitative definitions of entropy.[1]

Entropy is an extensive property and hence proportional to mass, but it should be noted that this does not mean that the entropy of a solution is the sum of the entropies of the components, as there will be an entropy change on mixing, as we shall see later (page 116).

Entropy Change in Irreversible Processes.—It must be emphasized that these definitions apply only to changes that are *completely reversible*. For a process that is not reversible, ΔS, or the change in entropy, is *not* equal to $\int dQ/T$. At first sight this seems like a serious limitation on the usefulness of the function because we are really interested in irreversible processes since all actual processes are irreversible, but as a matter of fact it is no limitation at all. Since entropy is a property, changes in its value are entirely independent of the actual way in which the process is executed but depend only on the terminal states of the process. Consequently, a reversible and an irreversible process between the same initial and final state have the *same entropy change*.

Calculation of Entropy Changes.—Some of the foregoing principles concerning the entropy function will now be illustrated by numerical examples.

Illustration 3.—What is the change in entropy when one pound-mole of an ideal gas at 70°F. and a pressure of 10 atm. abs. expands through a throttle to a pressure of 1 atm., both pressures being maintained constant during the process by suitable pistons? No external work, other than that against the constant-pressure pistons, is done.

This is clearly an irreversible process since the gas cannot be restored to its original pressure without causing some outside system to be run down. In an expansion of this type the gas will suffer no net temperature change. Local temperature changes will occur as a result of the conversion of internal energy into kinetic energy of mass flow; but when this energy has been dissipated, the net result will be an isothermal process.

Let us now proceed to calculate the change in entropy that accompanies this process. To do this we must first devise a reversible process between the same

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[1] It may be well to emphasize the fact that, whereas dQ/T is a perfect differential, dQ alone is not. There is no property Q, but there is a property whose derivative is dQ/T.

states. This is accomplished by placing the gas in a cylinder and compressing it slowly with a frictionless piston and removing the heat of compression as fast as it is formed by a suitable cooling device so that the gas is maintained at constant temperature. The conditions for reversibility in such a process have already been discussed in some detail in Chap. I. To calculate ΔS, Eq. (III.33) is used, and so we must first evaluate the heat effect for the compression. As will be shown later, E is zero for the isothermal compression of an ideal gas and therefore, by the first law, $W = Q$, or the work of compression equals the heat of compression when both are expressed in the same units. Now,

$$dW = p \, dv = dQ$$

and since $pv = RT$ for 1 mole of an ideal gas

$$dQ = RT \frac{dv}{v} = -RT \frac{dp}{p} \quad \text{(since } T \text{ is constant)}$$

$$\therefore \int_1^2 \frac{dQ}{T} = -R \int_{p_1}^{p_2} \frac{dp}{p} = -R \ln \frac{p_2}{p_1} = \Delta S$$

Substituting numerical values,

$$\Delta S = -1.987 \times 2.303 \log_{10} 10 = -4.571$$

The units of S will obviously be the same as those of R; and since we have expressed R in c.h.u. per pound-mole per degree centigrade, entropy will be in the same units.[1] There has been a decrease in the entropy of the gas of 4.571 units as a result of the reversible compression, and hence the irreversible expansion resulted in an *increase* in the entropy of the gas of the same amount.

Illustration 4.—What is the entropy change when 1,000 B.t.u. of heat flows by conduction from a constant-temperature reservoir at 212°F. to another one at 32°F.?

This irreversible heat flow could have been conducted in a reversible manner by allowing the heat to flow under a differential temperature difference from the reservoir at 212°F. to a fluid working medium in a Carnot engine. The engine will reject a smaller amount of heat to the lower temperature reservoir. The decrease in entropy of the hotter reservoir is $Q_1/T_1 = 1,000/(212 + 459.7) = 1.49$ B.t.u. per °R. From Eq. (III.24) it is seen at once that the entropy increase of the cooler reservoir is the same numerically as the entropy decrease of the hotter one, or in other words the net change in S for the whole process has been zero. This is characteristic of reversible processes when everything in which heat changes occur is included in the system. On the other hand, when the over-all transfer of heat was irreversible, the cooler reservoir received 1,000 B.t.u. at 32°F.; and since the actual transfer to the reservoir can be regarded as occurring under an infinitesimal temperature difference and therefore as reversible, the increase in entropy is $1,000/(32 + 459.7) = 2.03$ B.t.u. per °R. In other words, the over-all conduction process has resulted in an entropy increase of 0.54 unit.

Another way to regard this irreversible process is the following: Let the 1,000 B.t.u. of heat transferred to the lower temperature reservoir be restored by a reversible Carnot heat pump. This will make an entropy change of 2.03 units at both

[1] Numerically, this is the same as gram-calories per gram-mole per degree centigrade. Entropy units have received no name, but the unit in the metric system is frequently represented by the symbols E.U. (entropy unit). It is suggested that "clausius" would be an appropriate name for this unit.

reservoirs, but the heat discharged to the upper one will be the 1,000 B.t.u. plus the work done.   Thus,

$$Q_1 = Q_2 \frac{T_1}{T_2}$$

$$= 1,000 \frac{212 + 459.7}{32 + 459.7} = 1,365 \text{ B.t.u.}$$

Therefore, an excess of 365 B.t.u. is stored in the upper reservoir as a net result of the whole process consisting of the irreversible heat flow and the reversible heat pumping. This corresponds to an entropy increase of $365/671.7 = 0.54$ unit.

Illustration 5.—What is the entropy change when 1 lb. of dry air at atmospheric pressure is heated at constant pressure from 70 to 150°F.?

As long as we are interested only in the entropy change of the air itself and not in that of the system which is supplying heat to the air, we can imagine the actual transfer to the air to be from a substance that always differs in temperature from the air only by the amount dT; therefore, *as far as the air alone is concerned*, the heating process is reversible.

$$\therefore \Delta S = \int_1^2 \frac{dQ}{T}$$

In other words, the entropy change for any heating or cooling process is given by the expression for the entropy change of a reversible process as long as the temperature refers to that of the system under consideration and not to the surroundings.

For a constant-pressure process,

$$dQ = c_p \, dT$$

$$\therefore \Delta S = \int_{T_1}^{T_2} c_p \frac{dT}{T}$$

The integration is readily performed as soon as one can express c_p as a function of absolute temperature.   For the present purpose, assume c_p is a constant equal to 0.24 B.t.u. per lb. per °F.   Then,

$$\Delta S = 0.24 \ln \frac{T_2}{T_1} = 0.24 \times 2.303 \log_{10} \frac{150 + 459.7}{70 + 459.7} = 0.0338 \text{ B.t.u./(lb.)(°R).}$$

Illustration 6.—What is the change in entropy when 10 lb. of liquid water at 500°F. is mixed adiabatically with 30 lb. at 70°F.?

This is an irreversible process because there is no work obtained from the process that could be utilized to restore the initial state of the system.   Nevertheless, the cooling of the hot water can, by itself, be considered as taking place reversibly, and the same applies to the heating of the cold water (see Chap. I).   Therefore, the total entropy change is given by[1]

$$\Delta S = 10 \int_{500+460}^{t+460} c_p \frac{dT}{T} + 30 \int_{70+460}^{t+460} c_p \frac{dT}{T}$$

Assume c_p is constant and equal to unity.   From a heat balance,

$$10(500 - t) = 30(t - 70)$$
$$t = 177.5°F.$$

(Using enthalpy data from the Keenan-Keyes steam tables, $t = 182.3°F.$)

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[1] The water at 500°F. must be at an elevated pressure, but the effect of the pressure changes on the entropy may be neglected.

Solving the ΔS equation,

$$\Delta S = 10 \times 2.303 \log_{10} \frac{637.5}{960} + 30 \times 2.303 \log_{10} \frac{637.5}{530} = 1.44$$

(From the steam tables, $\Delta S = 1.55$.)

Illustration 7.—What is the entropy change for an isothermal chemical reaction? Consider the simple reaction

$$Hg(l) + \tfrac{1}{2}Cl_2(g) = HgCl(s)$$
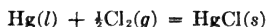
When this reaction is carried out at constant pressure in a calorimeter and referred to the constant temperature of 25°C., there is heat evolved to the extent of 31,300 cal. per mole of HgCl formed, or $\Delta H = -31,300$. Since this is a highly irreversible process, the entropy change cannot be obtained by dividing the heat evolved by the temperature at which it occurred. To calculate ΔS one must devise a reversible way to carry out the reaction. As was pointed out in Chap. I, a chemical reaction can be made reversible by carrying it out in an electrochemical cell in such a way that the maximum possible amount of electrical work is done. If a cell is set up in which the above reaction is the only one occurring, it will be found that the heat evolved at 25°C. is only 6,160 cal. per mole of HgCl formed. This is the reversible heat of reaction, and hence there has been an entropy decrease of $6,160/298 = 20.67$ g.-cal. per °C. The actual measurement is not the heat evolved but the e.m.f. of the cell, and from this the reversible heat of reaction can be calculated from the first law as follows:

$$\Delta E = Q - W$$

In the reversible process the work consists of two kinds, (1) the electrical work W_E and (2) the work done by the constant fluid pressure, $p \, \Delta v$

$$\therefore \Delta E = Q - W_E - p \, \Delta v$$
or
$$Q = \Delta H + W_E$$

The e.m.f. of a cell operating with this reaction at 25°C. $= 1.0894$ volts. Hence, $W_E = 1.0894 \times 23,074^* = 25,140$ g.-cal. per g.-mole.

$$\therefore Q = -31,300 + 25,140 = -6,160 \text{ cal.} \quad \text{(heat evolved)}$$

It may be noted that in some cases the reversible heat of reaction is of opposite sign to the ordinary calorimetric heat of reaction.

Entropy and Unavailable Energy.—When heat is transformed to work by means of a heat engine, we have seen that the transformation is never complete. A certain portion of the heat must be rejected to a refrigerator or heat receiver, and this portion must be regarded as unavailable for the production of work. The lower the temperature of the refrigerator, the smaller will be this unavailable portion; but the lowest practicable temperature of the refrigerator is that of the surrounding atmosphere or of any large body of water, which is substantially a heat reservoir of infinite size. It does no good to reject heat to any finite body at a lower temperature because this lower temperature would have to be maintained

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* The number of calories per volt equivalent.

and the work necessary to do this would be at least as much as that gained by the use of the lower temperature.

From Eq. (III.24) the unavailable heat Q_0 is equal to $Q_1(T_0/T_1)$, where Q_1 is the total quantity of heat taken into the engine and T_1 and T_0 are the absolute temperatures of the source and refrigerator, respectively. If the heat is taken from a fluid during a change of state of the fluid so that, in general, the temperature T_1 may be continually changing (this amounts to regarding the heat as being transferred from a finite instead of an infinite heat reservoir), this equation may be generalized to

$$\frac{Q_0}{T_0} = \int_1^2 \frac{dQ}{T} \tag{III.34}$$

or

$$Q_0 = T_0 \int_1^2 \frac{dQ}{T} \tag{III.35}$$

$$= T_0\, \Delta S \tag{III.36}$$

since $\int_1^2 dQ/T$ is the entropy change of the fluid, which is transferring heat during a change of state. We may state the result expressed by Eq. (III.36) in the following way: Whenever a quantity of heat is transferred to or from a fluid during a reversible change of state, the portion of this heat that is unavailable for transformation to work in a cyclic process is equal to the change of entropy accompanying the given change of state multiplied by the lowest available absolute temperature at which large quantities of heat can be rejected. There is, therefore, a direct proportionality between the entropy change of such a process and the unavailable heat energy. From Eq. (III.36) the unavailable heat is readily calculated for any given state change, once the properties of the fluid involved are known.

The concept of unavailable energy is also useful in dealing with irreversible processes. When such a process takes place, it is said that some energy has become "unavailable" for work. Let us assume that a measure of the unavailable energy change for the process is given by the minimum work necessary to restore the whole system to the state that existed before the irreversible change occurred. In order to restore it, work must be done on it, and if this work is to be a minimum the restoring process must be assumed reversible. Let this work be represented by W_0. Since the system is restored to its initial state, its $\Delta E = 0$ and therefore the work W_0 must appear as heat Q_0 in a heat reservoir. The only receiver to which we can continue to reject unlimited amounts of heat without appreciable effect on the temperature is the atmosphere or a large body of water at a temperature T_0. (Incidentally, if this heat were rejected to a reservoir at any temperature above T_0, the lowest temperature of the surroundings, the possibility would exist of obtaining

more work, so that for minimum work the heat is rejected at T_0.) The entropy increase of this reservoir is $\Delta S_0 = Q_0/T_0$, and this is also equal to the ΔS of the system since the restoring process is assumed reversible. Consequently, the restoring work $= Q_0 = T_0 \Delta S$. Thus we see that this concept of unavailable energy leads to the same mathematical expression as the previous case.

To summarize, unavailable energy may be defined as the product of an entropy change and the absolute temperature T_0 of a heat reservoir at the lowest natural temperature of the surroundings. When applied to a change of state involving heat transfer, it will mean that portion of the heat which must be rejected to the heat reservoir at T_0, assuming the heat were to be transformed to work in a heat-engine cycle. When applied to an irreversible process, it will mean the least amount of work that would be necessary to restore the system to the state in which it existed before the irreversible process occurred.

A few numerical examples may help to clarify some of these ideas.

Illustration 8.—One pound of water is heated at the constant pressure of 200 lb. per sq. in. abs. from 70°F. to the boiling point and then completely vaporized at this pressure. What portion of the heat transferred is unavailable for transformation to work in a heat engine, assuming 50°F. as the lowest constant temperature at which heat can be rejected?

Values for the properties of steam will be obtained from the Keenan-Keyes tables.[1]

Boiling point at this pressure $= 381.8°F.$
Latent heat of vaporization $= 843$ B.t.u. per lb.

$$\text{Total heat transferred} = \int_{T_1}^{T_2} c_p \, dT + L$$

where $L =$ latent heat of vaporization.

This sum can be obtained directly from the steam tables by taking enthalpy differences, assuming the enthalpy of the liquid is independent of pressure. Thus,

H_2 (enthalpy in final state) $= 1,198.4$
$H_1 = 38.0$
$\Delta H =$ heat transferred $= 1,160.4$

$$\text{Change in entropy} = \int_1^2 \frac{dQ}{T} = \int_{T_1}^{T_2} c_p \frac{dT}{T} + \frac{L}{T_2}$$

This sum can also be read directly from the steam tables as a difference of two entropies.

$S_2 = 1.5453, \qquad S_1 = 0.0745$
$\Delta S = S_2 - S_1 = 1.4708$
Unavailable energy $= T_0 \Delta S = (50 + 460)1.4708 = 750$ B.t.u.

$(750/1,160) \times 100 = 64.8$ per cent of the heat transferred to the water is unavailable for conversion to work.

Illustration 9.—Suppose that the heat to vaporize the water in Illustration 8 has been transferred from a furnace at a temperature of 2200°F. This represents an entropy decrease of $1,160/(2,200 + 460) = 0.436$ unit.

[1] KEENAN and KEYES, *op. cit.*

The entropy increase of the water was 1.471, and therefore the net entropy increase due to the irreversible heat transfer $= 1.471 - 0.436 = 1.035$.

The increase in unavailable energy accompanying this transfer, with respect to a heat receiver at 50°F., is

$$T_0 \, \Delta S = 510 \times 1.035 = 527 \text{ B.t.u.}$$

This quantity of energy may be interpreted either as (1) the difference between the work obtainable from a reversible engine operating between a constant heat source at 2200°F. and a heat reservoir at 50°F. and the work obtainable from a reversible engine receiving heat from water as it changes state from that of saturated steam at 200 lb. per sq. in. to that of water at 70°F. and rejecting heat at 50°F. or (2) the least amount of work necessary to restore the system to its initial state, leaving only changes elsewhere and rejecting heat only at 50°F.

The increase in unavailable energy as a result of any one of the irreversible processes considered on pages 26 and 27 is obtained at once by multiplying the calculated entropy change by an assumed temperature T_0 of a heat receiver. In the case of Illustration 3 (page 68), $\Delta S = 4.571$; and, for a heat-receiver temperature of 32°F., the energy rendered unavailable $= 492 \times 4.571 = 2,250$ B.t.u. per lb.-mole. If the expansion had been performed at 200°F. instead of 70°F., the unavailable energy, according to our accepted definition, would have been just the same. Nevertheless, the amount of work obtainable from the reversible expansion would have been different in the two cases. Thus, from the equations in Illustration 3, it is evident that

$$W = RT \ln \frac{p_2}{p_1}$$

and therefore the lost work is proportional to the absolute temperature at which the isothermal expansion takes place.

Some authorities have attempted to define change in entropy as the ratio between the unavailable energy chargeable to the process and the absolute temperature of a heat receiver at the lowest temperature of the surroundings. There would seem to be little justification for this because there is no definite and unambiguous definition of unavailable energy that is applicable to all the various processes with which we shall be concerned. On the other hand, entropy is the more fundamental concept, and it can be clearly defined by a very simple relation. It is much better, therefore, to define increase in unavailable energy on the basis of entropy rather than to attempt to reverse the process.

Availability.—Consider 1 lb. of any substance in a given state and assume that the substance is to act as a heat reservoir giving up heat to a reversible heat engine. The engine receives heat at the variable temperature T equal to the temperature of the substance at any instant but rejects heat always at the lowest available temperature T_0. The maximum work obtainable from the heat given up by such a source is

given by the expression, based on the Carnot principle [see Eq. (III.20)][1],

$$W = -Q \frac{T - T_0}{T} \tag{III.37}$$

or, using differentials, since in general only an infinitesimal amount of heat is received at any one temperature level,

$$W = - \int_{T_1}^{T_0} \frac{T - T_0}{T} \, dQ \tag{III.38}$$

$$= - \int_{T_1}^{T_0} dQ + T_0 \int_{T_1}^{T_0} \frac{dQ}{T} \tag{III.39}$$

$$= - \left[Q - T_0 \, \Delta S \right]_{T_1}^{T_0} \tag{III.40}$$

The term $T_0 \, \Delta S$ is what has just previously been designated as the "unavailable" energy. The interpretation of this equation is very simple. For the change in question, Q, the total heat transfer, consists of two parts, one of which, $T_0 \, \Delta S$, is unavailable for work and the other of which can, in an ideal engine, be completely transformed to useful work.

If the state change of the substance is one at constant pressure, (Eq. III.40) becomes

$$W = - \left[\underline{\Delta H} - T_0 \, \Delta S \right]_{T_1}^{T_0} \tag{III.41}$$

In this particular case the work is a function of the initial state of the substance (for a given receiver temperature T_0) and hence is analogous to a property, which has been given the name of "availability" and is represented by the symbol B. It has recently become popular in certain types of thermodynamic analysis. For any change in state of a substance from state 1 to state 2, the change in availability is given by

$$-\Delta B = \left[\Delta H - T_0 \, \Delta S \right]_{T_1}^{T_2} \tag{III.42}$$

Keenan[2] has given a somewhat more general definition of the availability function for a nonflow process. He considers it to be the maximum useful work that a substance in a given state could do by virtue of acting not only as a heat source for reversible Carnot heat engines but also as a result of its own pv changes. When both the pressure and the temperature are reduced to the dead level of that of the surroundings, no further potential or driving force for work exists. The maximum possible work resulting from these two effects between an initial state p_1, T_1 and the dead state p_0, T_0 is

$$W = - \int_1^0 \frac{T - T_0}{T} \, dQ + \int_1^0 p \, dv \tag{III.43}$$

[1] Q refers to the heat given up by the substance and hence is negative.
[2] KEENAN, J. H., *Mech. Eng.*, **54**, 195–204 (1932).

but of this total the amount $p_0 \, \Delta v$ is merely work against the atmosphere and cannot be counted as useful work.   Hence, the net work or availability is given by

$$B = -\int_1^0 \frac{T - T_0}{T} \, dQ + \int_1^0 p \, dv - p_0 \, \Delta v \qquad \text{(III.44)}$$

$$B = -\int_1^0 dQ + \int_1^0 T_0 \, dS + \int_1^0 p \, dv - p_0 \, \Delta v \qquad \text{(III.45)}$$

$$B = -Q + T_0(S_0 - S_1) + \int_1^0 p \, dv - p_0(v_0 - v_1) \qquad \text{(III.46)}$$

By the first law,

$$\Delta E = E_0 - E_1 = Q - \int_1^0 p \, dv$$

$$\therefore \ B = -(E_0 - E_1) + T_0(S_0 - S_1) - p_0(v_0 - v_1) \qquad \text{(III.47)}$$

$$B = (E_1 + p_0 v_1 - T_0 S_1) - (E_0 + p_0 v_0 - T_0 S_0) \qquad \text{(III.48)}$$

This is clearly a function of state 1 and hence a property, if p_0 and T_0 are fixed.

The change in availability in going from state 1 to state 2 is given by

$$\Delta B = (E_2 + p_0 v_2 - T_0 S_2) - (E_1 + p_0 v_1 - T_0 S_1) \qquad \text{(III.49)}$$

It is somewhat confusing to have these two definitions of the availability function; but as a matter of fact the availability is applied mainly to continuous-flow systems, and for such systems the Keenan availability as defined by Eq. (III.48) reduces to the simpler one defined by (Eq. III.41) when kinetic- and gravitational potential-energy effects are neglected.

Illustration 10.—A proposed solar engine will absorb radiation from the sun in an organic liquid that will rise in temperature from 200 to 300°F. at constant pressure.   What is the maximum per cent of the radiant energy absorbed that is available with reference to a temperature of 60°F. of the surroundings?

Total energy absorbed per pound of liquid $= \Delta H = c_p(T_2 - T_1)$
Change in availability $= \Delta H - T_0 \, \Delta S$

$$= c_p \left[(T_2 - T_1) - T_0 \ln \frac{T_2}{T_1} \right]$$

Fraction available $= 1 - \dfrac{T_0}{T_2 - T_1} \ln \dfrac{T_2}{T_1}$

$$= 1 - \tfrac{520}{100} \times 2.303 \times \log \tfrac{760}{660}$$

$$= 0.269$$

Aside from its quantitative application, the idea of available energy is a very convenient one in describing certain effects.   For example, certain forms of energy, such as the kinetic energy of mass motion, are completely (100 per cent) available for doing work in a perfect device, but in the actual conversion process there is a loss in the sense that only a fraction (say 70 per cent) of the possible work is actually obtained.

The 30 per cent does not represent a loss in energy because according to the first law no energy can be lost.   Nevertheless, it is a loss in the second-law sense and one refers to it as a loss in available energy.

Entropy Changes in Isolated Systems.—There can be no completely isolated system in a practical sense; but the concept of such a system, like that of the reversible process, is a useful tool in analysis.   We shall define the isolated system as one that includes all material bodies in which any changes occur connected with a particular change on which attention has been focused.   Strictly, this includes the whole universe, and this is the only true isolated system; but, for practical purposes, we can arbitrarily select a far more limited system.   A concrete illustration may make this much clearer.   Suppose that a chemical reaction were taking place in a closed container of constant volume, which was placed in a thermostat.   If the latter were well insulated from the surroundings so that little heat interchange took place, then the combination of reaction vessels plus thermostat would constitute a close approach to an isolated system.

The material that constitutes the chemically reacting system itself will be referred to as the "particular system" to distinguish it from the isolated system, which includes the thermostat as well.   If the reaction is taking place in an electrochemical cell and yielding an e.m.f., then the whole electrical system external to the reacting vessel must be included in the isolated system.   A factory room with all doors and windows closed, in which some machines were being operated by electrical energy obtained from a storage battery, would be an isolated system except for the small interchange of heat and light with its surroundings.

The true isolated system is one around which we could draw an enveloping surface and no material or energy would cross this surface. Strictly, of course, such a system could not be placed under observation because the very act of observing interferes with the isolation.   Nevertheless, the concept of such a system has proved useful in thermodynamic reasoning and has led to results of broad application, as we shall later show (page 82).   Our so-called "isolated" system will, in general, contain three things, (1) particular systems in which state changes occur; (2) heat reservoirs, large enough so that no state changes occur; and (3) work-doing mechanisms.

If the particular system under consideration is the working substance of a heat engine operating on the Carnot cycle, then the isolated system must include both the heat reservoirs and the work-doing mechanism. It is not necessary to specify in detail the nature of the work-performing mechanism which we shall assume, for simplicity, to cause the raising of a weight and to operate in a frictionless manner.   This will involve no entropy change.   Entropy changes will occur in the working substance

and in the two heat reservoirs. If the working substance and the reservoirs are always at the same temperature when exchanging heat, an increase in S of working substance will be exactly compensated by a decrease in S of a reservoir, and vice versa.   If the engine itself is reversible, no entropy changes will be involved because the action of any directive force involves no entropy change unless friction (or analogous resistances) is present.   Consequently, we conclude that in any isolated system in which a reversible Carnot engine is operating the total entropy remains constant.

This result can readily be generalized for a more complex cycle.   It is clear that $\Delta S = 0$ for the working substance (the particular system) since it goes through a cycle of changes.   Every increase in S of the working substance will be exactly compensated by a decrease in S of a heat reservoir, and vice versa, provided that the whole process is reversible.   This means that the working substance never differs more than an infinitesimal amount in temperature from any reservoir with which it is exchanging heat and so $\int dQ/T$ is bound to be the same numerically for both, but of opposite sign.   The reasoning need not be restricted to the case of a complete cycle of changes.   It holds just as well for any change that does not return the particular system to the original state.   To sum up: In any isolated system in which nothing but reversible processes take place, the entropy remains constant.
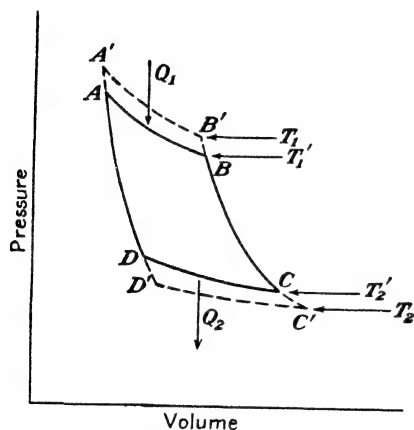
FIG. III.4.—Irreversibility in a heat-engine cycle.

Now let us consider a case in which there is some irreversible process occurring.   For ease of visualization we shall consider the simple Carnot cycle, bearing in mind that the same ideas apply to a more complex case.

In Fig. III.4 let $ABCD$ represent the cycle of changes through which the working substance passes.   It receives heat Q_1 along the T_1' isotherm, but from a heat source at the constant temperature T_1.   Similarly, the working substance rejects heat Q_2 along isotherm DC at T_2', but it flows to the reservoir at T_2.   The two heat flows under a finite temperature difference constitute irreversible effects.   That such a process as a whole is irreversible is graphically shown by the fact that the work done, represented by the area $ABCD$, is less than the maximum possible work which could be done—the area $A'B'C'D'$.   The heat reservoir at T_1

suffers an entropy decrease of Q_1/T_1 units and that at T_2 an increase of Q_2/T_2 units. Since the working substance itself passes through a complete cycle, its ΔS must equal 0, or

$$\frac{Q_1}{T_1'} - \frac{Q_2}{T_2'} = 0$$

Since $T_1 > T_1'$ and $T_2' > T_2$, then $-(Q_1/T_1') + (Q_2/T_2) > 0$ and the net result of the whole process in the isolated system (the raising of the weight involving no entropy change) is *an increase in entropy.*[1]

Instead of taking an irreversible heat flow we could consider the case of friction in the engine. A similar process of reasoning would have led to an identical result—a net increase in entropy.

Various other examples could be chosen involving other types of irreversible changes such as gas expansion without performance of useful work, mixing of two gases, chemical reaction without performance of electrical work, vaporization of a superheated liquid, solution of a solid in a liquid, and stirring of a liquid; but it is unnecessary to deal further with special cases since we can generalize our reasoning to apply to any irreversible process. From the discussion of irreversible processes in Chap. I it is evident that whenever such a process occurs the particular system involved can be wholly restored to its initial state *only by the use of work from some outside system.* Now imagine any isolated system in which one or more processes occur in particular systems and with some irreversibility, however slight. The work that is done may be of various kinds but will be assumed to result eventually in the purely mechanical work of raising weights. Transfers of heat will also have occurred between particular systems and heat reservoirs all within the isolated system. By allowing the weights to fall the systems can be partly restored to their initial states but not wholly if there was any irreversibility.

Let us now assume that we had in the general environment composing part of the isolated system a raised weight which can now be lowered to do the work necessary to restore all the particular systems to their initial states. With all systems (exclusive of heat reservoirs) returned to their initial state, $\Delta E = 0$ and $\Delta S = 0$; therefore, the work done will appear as heat in a reservoir, and this involves *an increase in entropy.* Thus the net result of the irreversible process in the isolated system was an increase in the entropy of the system as a whole.

The statement is sometimes made that entropy always increases in any irreversible process. This is a loose statement that is incorrect unless

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[1] The walls separating the heat reservoirs and working fluids would in any actual case involve some entropy changes, especially since they are alternately heated and cooled, but in the ideal case we are assuming that these changes are negligible. This amounts to an assumption that the walls have a negligible heat capacity.

qualified.   Many chemical reactions occur irreversibly with a decrease in entropy as far as the reacting system itself is concerned, but there is always a more than compensating increase in the entropy of the surroundings so that for the *isolated* system (chemically reacting system plus surroundings) the net result is always an increase in entropy.

General Mathematical Statement of the Second Law.—Clausius has epitomized this whole concept in his famous statement *Die Entropie der Welt strebt einem Maximum zu.*   We may summarize all our discussion of the entropy function by the following concise statement in mathematical language:

$$dS \gtreqless 0 \quad \text{for isolated systems} \quad \text{(III.50)}$$

For any reversible change, of infinitesimal amplitude, in an isolated system, the total entropy remains unchanged; but, for any change involving an irreversible effect, the total entropy increases.

Equation (III.50) is the epitome of all our discussion of the second law of thermodynamics and is the most general quantitative statement of it that can be made.   It also furnishes the most general criterion of equilibrium and of tendency toward spontaneous change.

Numerical Values of Entropy.—Entropy has dimensions of energy divided by temperature, and various units are possible, depending on how the energy is expressed and what temperature scale is used.   We shall generally express entropy as B.t.u. per pound (or pound-mole) per degree Fahrenheit or c.h.u. per pound (or pound-mole) per degree centigrade.   The latter unit is identical with gram-calories per gram (or gram-mole) per degree centigrade.

In many problems one is concerned only with entropy differences without regard to an absolute value, and in such cases it is customary to choose $S = 0$ at any convenient datum point such as 32°F. and 1 atm. pressure.   As a result of the studies that have culminated in the third law of thermodynamics, which will be discussed briefly in Chap. XI, it is possible to assign an absolute value to entropy, and such values are essential in the complete treatment of chemical equilibrium.

Physical Meaning of Entropy.—A comprehensive discussion of this would lead us too far afield, but a brief one may be worth while since a better visualization of the physical meaning of this once mysterious quantity may help in its application.   We have seen from the discussion in Chap. II that an underlying reason for irreversibility is the fact that in all irreversible processes the system has passed from a state of low probability to one of higher probability or from a more orderly arrangement to a less orderly or more chaotic one and the chances of an unshuffling to reproduce the initial state are infinitesimally small because of the very large number of individuals involved.   Consider the simple case of two portions of a given gas at different temperatures.   When the two

are connected thermally, one gas cools and the other heats until an equilibrium state is reached, represented by an equality of the two temperatures. We know from experience that this system will never again develop a temperature difference by itself, *i.e.*, spontaneously. From the kinetic theory we know that the gas at uniform temperature really consists of molecules that at any instant differ greatly in their velocities and therefore in kinetic energy. There are "hot" molecules (high speed) and "cold" molecules (low speed) and all gradations in between. As we have seen from the analogy to a deck of cards, the most probable arrangement is one of complete shuffling of all the different kinds of molecules (*i.e.*, differing as to velocity) for the simple reason that the number of highly shuffled or mixed-up arrangements is enormously greater than the number of configurations in which there is an approach to an orderly arrangement. Any arrangement in which the hot molecules would preponderate to a sufficient extent to permit an observable difference in temperature between any macroscopic portions of the gas would be so improbable as to be nonexistent.

What is the relation of all this to entropy? Simply that entropy is a measure of "mixed-upness" or of the probability of a given state. The more completely shuffled any system is, the greater is its entropy; and, conversely, an orderly or unmixed configuration is one of low entropy. This gives us a definite clue to the fact that entropy should have a zero value and is an absolute quantity. When a substance reaches a state in which all randomness has disappeared, it should then have zero entropy. A pure crystalline substance at the absolute zero of temperature would seem to fulfill this requirement and so it should have zero entropy (except possibly for any randomness that might be considered to exist in the internal structure of the atoms themselves).

By application of the theory of probability to molecular systems, to which it should apply rigorously because of the enormous number of individuals involved, Boltzmann showed that there was a simple relationship between the entropy of a given system of molecules and the probability of its occurrence. The derivation of this relationship and its further elaboration to permit the calculation of absolute entropies are beyond the scope of this text.[1]

Combined Statement of the First and Second Laws.—In Eq. (III.50) S refers to the entropy of an isolated system, *i.e.*, a particular system plus its immediate surroundings, to take a simple case. In any thermodynamic analysis we wish to focus attention on a particular system and

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[1] The reader who wishes to pursue this subject further is referred to Chap. XVII of "A Treatise on Physical Chemistry," edited by H. S. Taylor, D. Van Nostrand Company, Inc., New York, 1931, or to Chap. VIII of "Introduction to Theoretical Physics," by L. Page, D. Van Nostrand Company, Inc., New York, 1928.

omit the surroundings from consideration.   To do this the total entropy may be divided into two parts, S, the entropy of the particular system under study, and S', the entropy of all the environment that must be included to make it an isolated system.   Equation (III.50) then becomes

$$dS + dS' \lesseqgtr 0 \qquad (III.51)$$

Any interchange of energy between the particular system and its environment must consist either of the transfer of heat or of the doing of work through the action of some force (we are assuming no transfer of material between the two).   Since we are not interested in detail in what occurs in the environment, for purposes of analysis we are justified in assuming the simplest case, *viz.*, that all changes in the environment are reversible. Therefore, the entropy of the environment can be changed only by a heat transfer, or one can write

$$dS' = \frac{-dQ}{T'} \qquad (III.52)$$

The minus sign before dQ means that the heat is referred to the particular system and heat flow from a system has been taken to be negative.   By the first law,

$$dQ = dE + dW$$

Substituting this in Eq. (III.52),

$$dS' = \frac{-dE - dW}{T'} \qquad (III.53)$$

If we assume that all heat flows between the system and its surroundings are reversible, which we may do since we are not concerned about the details of what occurs in the surroundings, then

$$T = T' \qquad (III.54)$$

where T is the temperature of the particular system at any instant. From a combination of Eqs. (III.51), (III.53), and (III.54),

$$dS - \frac{dE + dW}{T} \lesseqgtr 0 \qquad (III.55)$$

$$T\, dS - dE - dW \lesseqgtr 0 \qquad (III.56)$$

All quantities in this equation refer to the particular system, dS and dE being its increase in entropy and energy, respectively, and dW the work done by the system.   The equality is true for a completely reversible process occurring in the system, and the inequality refers to a change that includes some irreversible effect, no matter how small or how great. This is probably the most significant equation in the whole book; for it is a combined statement of the two fundamental laws, and all subsequent relationships will be based on it.   In a sense, it contains in itself all the fundamental thermodynamic basis for the whole treatment to follow

except for those applications which involve the third law. There is probably no other equation ever developed that contains as many possibilities for wide application as this one.

THE WORK FUNCTION

Equation (III.56) is not, in general, integrable because $T \, dS$ and dW are not perfect differentials. In order to integrate it to apply to a change of finite amplitude, it would be necessary to express dW in terms of properties along some particular path and also to know how S and T were related. Transposing dW and changing signs,

$$dE - T \, dS \gtreqless -dW \qquad \text{(III.57)}$$

For the special case of an isothermal change, the left-hand side of this equation is the differential of the function $E - TS$, as can easily be verified by differentiating the expression for the function at constant temperature. This function, represented by the symbol A, was called "free energy" by Helmholtz. This term was later applied to another and more generally useful function by G. N. Lewis, and most authors have adopted this change. Many German authors still use the older nomenclature, and this has resulted in some confusion. The function A is commonly called "maximum work," but this is somewhat unfortunate because, depending on the direction of a change, it may measure the minimum work. Furthermore, the so-called "net" work measured by the change in free energy, ΔF, *may be greater than the maximum work*, as will be shown presently (page 86). For these reasons we have adopted the term "work function" for A. There is no ambiguity in regard to it if it is understood that change in A is equal to the algebraic summation of all work terms involved in the isothermal change.

By definition, $A = E - TS$ (III.58)
At constant T, $dA = dE - T \, dS \gtreqless -dW$ (III.59)
Integrating,
$$A_2 - A_1 = (E_2 - TS_2) - (E_1 - TS_1) \gtreqless -\Sigma W \qquad \text{(III.60)}$$

The symbol ΣW is used to indicate that more than one work term may be involved, depending on the forces acting, and ΣW represents their algebraic summation. For example, there might be work due to action of a fluid pressure and also to an e.m.f., and the two may be of opposite sign.

Equation (III.60) states that, when any system undergoes a reversible change at constant temperature, the total work done *by* the system (plus work) is equal to the decrease in A, whereas, if the change is isothermal but not reversible, the work done is less than the decrease in A. This may be a little clearer if Eq. (III.60) is put into the form

$$A_1 - A_2 \lesseqgtr \Sigma W \qquad \text{(III.61)}[1]$$

If $A_1 > A_2$, there is a decrease in A and work is done by the system. From this it is evident that A is a measure of the *maximum* work which a system can perform when it undergoes an isothermal change in such a direction that it does work on the surroundings.   If we knew the values of E and of S for various possible states, it is obvious that we should be in a position to predict the *maximum* work obtainable for any proposed change, provided always that it is isothermal.

It is true, of course, that A is a property, and there is a definite change in A for any given state change *whether isothermal or not;* but only for an isothermal change does ΔA give a measure of the work.

Conversely, when external forces are applied to do work on a system, resulting in a change of state, then the *minimum* work required to bring about the change is measured by the increase in A for the system [see Eq. (III.60)].   The minimum work will be for the reversible case, and for an irreversible process it is readily seen from Eq. (III.60) that the work will be greater than the increase of A for the system.

Rearranging Eq. (III.60),

$$(E_2 - E_1) - T(S_2 - S_1) \gtreqless -\Sigma W \qquad \text{(III.62)}$$

and
$$(E_1 - E_2) - T(S_1 - S_2) \lesseqgtr \Sigma W \qquad \text{(III.63)}$$

$E_2 - E_1$ is the total energy change accompanying the given process, and $T(S_2 - S_1)$ is the heat effect if the process is conducted reversibly. From Eq. (III.63) it is readily seen that the maximum work which the process is capable of yielding may be greater or less than the total energy change, depending on the sign of S.   If the entropy of the system decreases as a result of the change, then $T \Delta S$ is positive and heat will be transferred out of the system to the thermostat and the work will be less than the energy decrease.   On the other hand, if the entropy increases, heat will be transferred to the system from the thermostat and the work done is greater than the total energy change by the amount of this heat.

In the case of a chemical reaction, ΔE is generally much greater numerically than $T \Delta S$ so that ΔA is generally of the same sign as ΔE and of the same order of magnitude.   This fact may be useful for rough approximations of the work or of equilibria in the absence of any entropy data.   Of course, for the special case where there is no entropy change,

$$\Delta A = \Delta E$$

and equilibria can be quantitatively predicted from changes in E.

If the process is not reversible, the heat effect may be quite different and even of the opposite sign.   For example, in the case where the

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[1] Note that changing the signs on both sides of an inequality changes the direction of the inequality.

entropy increases, heat flows into the system when the process is reversible, all the ΔE being converted to work. If irreversible, some of the ΔE will not be converted to work and so must appear as heat given to the thermostat and this amount of heat may be greater than the reversible, or $T \Delta S$, heat, with the result that there is a net evolution of heat rather than an absorption. For example, the reaction

$$Pb(s) + 2HgCl(s) = PbCl_2(s) + 2Hg(l)$$
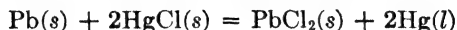
will proceed with a heat absorption of 1,990 cal. if carried out reversibly and isothermally in a galvanic cell; but if carried out isothermally in a calorimeter with no opposing e.m.f., it will evolve 22,730 cal. (all heats are for 25°C.).

It may seem at first thought somewhat paradoxical and contrary to the second law that heat added to a system from a thermostat is completely converted to work as is the case in a chemical reaction for which S increases or in the reversible isothermal expansion of a gas. In this latter case, $\Delta E = 0$ if the gas is ideal, and all the work is due to the heat effect $T \Delta S$. However, let us emphasize that there is nothing contrary to the second law in the complete conversion of heat to work in any process *which is not cyclic*. For a physical interpretation of this, one can regard the work as resulting, not from the energy of the random motion of molecules, which is completely unavailable in the absence of a temperature difference, but from a potential energy due to directed forces in the material; as this energy is converted to work, the temperature would tend to fall, but this is compensated by a heat flow from the thermostat. Now, if the process were conducted in a cycle so that there could be no net energy change for the system, then no net work could be done unless there was a temperature difference. In other words, the total net work is zero in any isothermal reversible cycle. This result is readily deduced from Eq. (III.60) because for a cycle ΔA must be equal to 0 and therefore ΣW equals 0. This deduction is of considerable historical importance, for it formed the basis for several important derivations.

THERMODYNAMIC POTENTIAL OR FREE ENERGY

In the previous section we considered a special type of change, *viz.*, an isothermal one, and found that a certain function A was particularly useful in such a case. Now we shall consider another special case of even greater practical importance, *viz.*, one at both constant temperature and constant pressure. Many changes of practical importance do occur under approximately these conditions, the constant pressure frequently being that imposed by the atmosphere. For such a case it is convenient to divide the algebraic total work ΣW into two parts, (1) that done by the constant fluid pressure, or $p \, dv$ for an infinitesimal displacement; and

(2) the work against other forces, sometimes called "net" work, represented by W'. Thus,

$$dW = dW' + p\,dv \qquad \text{(III.64)}$$

or, for a finite change,

$$\Sigma W = W' + p\,\Delta v \qquad \text{(III.65)}$$

In the case of a chemical reaction conducted in a cell, W' is the electrical work and $p\,\Delta v$ is the mechanical work done by or against the atmosphere or other constant fluid pressure. A little confusion may result from the terms commonly used to describe ΣW and W' because, depending on the sign of Δv, the net work W' may be greater or less than the total work ΣW. As long as there is an increase in volume accompanying the doing of useful work by the system, the interpretation is clear; but when the volume decreases as in the reversible cell producing liquid water from hydrogen and oxygen, the so-called "maximum" work, $-\Delta A$, is 55,670 g.-cal. per mole at 25°C., whereas the "net" work, or $-\Delta F$, is 56,560 cal.

Substituting Eq. (III.64) in Eq. (III.57) and transposing $p\,dv$,

$$dE - T\,dS + p\,dv \gtreqless -dW' \qquad \text{(III.66)}$$

for an isothermal, isobaric (constant-pressure) process. Since p and T are both constant, the left-hand term of this equation is a perfect differential, the function being $E - TS + pv$, usually represented by F. This function was first extensively applied by Gibbs and was called by him "thermodynamic potential." G. N. Lewis applied the name "free energy" (originally used by Helmholtz for A), and this nomenclature has been adopted by most American and English authors.

Integrating Eq. (III.66), $\Delta F \gtreqless -W'$ (III.67)

Stated in words, ΔF, or the change in free energy, is a measure of the net work in an isothermal, isobaric change that is reversible. In one direction it measures the maximum useful work that could be delivered as a result of the change, and in the other direction it measures the minimum net work required to accomplish the change. If there is any irreversibility connected with the change, the work will be less in the one direction and more in the other. Other forms of Eq. (III.67) may be written as follows:

$$\Delta F = E_2 - E_1 - T(S_2 - S_1) + p(v_2 - v_1) \gtreqless -W' \qquad \text{(III.68)}$$
$$\Delta F = A_2 - A_1 + p(v_2 - v_1) \gtreqless -W' \qquad \text{(III.69)}$$
$$\Delta F = H_2 - H_1 - T(S_2 - S_1) \gtreqless -W' \qquad \text{(III.70)}$$

The maximum (or minimum) work for any process conducted at constant pressure and temperature can therefore be predicted if the values of E, S, and v for the initial and final states are known, and it will be independent of the actual mechanism employed to bring about the change.

If there is no volume change, ΔF will equal ΔA; and since the term $p \, \Delta v$ is usually relatively small, ΔF will be approximately equal to ΔA in nearly all cases.

FUNDAMENTAL DIFFERENTIAL EQUATIONS

Special Conditions Imposed.—To make convenient application of the functions that have been defined in this chapter, certain equations are required that relate the functions to the ordinary variables of state. It will be the purpose of this section to derive such equations; the derivation will be purely a matter of elementary mathematical manipulations, for all the fundamental principles have already been introduced in defining the functions. For the present, we shall restrict the derivations to the special case of (1) homogeneous systems containing only one component (or multicomponent systems of substantially constant composition such as air); (2) the only force acting is a uniform fluid pressure; and (3) systems in equilibrium. (In the next chapter the equations will be generalized to apply to more complex systems.) For this case, the state of the system can be represented by an equation (commonly called "equation of state") whose general form is

$$\phi(p,V,T,m) = 0 \tag{III.71}$$

or, for a given constant mass m, the state is completely defined by two independent variables, thus,

$$p = \phi(V,T)$$

with similar equations using another set of two independent variables.

Equations for E and S in Terms of v and T.—Since the state is defined by two variables, E, H, S, or any of the functions or thermodynamic properties may be expressed in terms of two independent variables, as, for example,[1]

$$E = \phi(T,v)$$

From the well-known methods of calculus reviewed in Chap. I,

$$dE = \left(\frac{\partial E}{\partial T}\right)_v dT + \left(\frac{\partial E}{\partial v}\right)_T dv \tag{III.72}$$

but, by the first law, $\qquad dQ = dE + p \, dv^*$

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[1] In the remainder of the chapter, all extensive properties such as volume and energy will be on the basis of a molal mass or a unit mass.

* From all the equations in this chapter the mechanical equivalent of heat J has been omitted. The first-law equation should strictly be written

$$dQ = dE + \frac{1}{J} p \, dv$$

if E is measured in thermal units. When one comes to apply the equations to numerical problems, he must be careful to insert J at the proper point.

$$\therefore \; dQ = \left(\frac{\partial E}{\partial T}\right)_v dT + \left[\left(\frac{\partial E}{\partial v}\right)_T + p\right] dv \tag{III.73}$$

By the second law, $\qquad dS = \dfrac{dQ}{T}$

Substituting from Eq. (III.73),

$$dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_v dT + \frac{1}{T}\left[\left(\frac{\partial E}{\partial v}\right)_T + p\right] dv \tag{III.74}$$

$$\therefore \; \left(\frac{\partial S}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_v \tag{III.75}$$

and $\qquad \left(\dfrac{\partial S}{\partial v}\right)_T = \dfrac{1}{T}\left[\left(\dfrac{\partial E}{\partial v}\right)_T + p\right]$ (III.76)

Now utilize the fact that

$$\frac{\partial^2 S}{\partial T\,\partial v} = \frac{\partial^2 S}{\partial v\,\partial T} \tag{I.19}$$

Then $\quad \dfrac{1}{T}\left(\dfrac{\partial^2 E}{\partial T\,\partial v}\right) + 0 = \dfrac{1}{T}\left[\dfrac{\partial^2 E}{\partial v\,\partial T} + \left(\dfrac{\partial p}{\partial T}\right)_v\right] - \dfrac{1}{T^2}\left[\left(\dfrac{\partial E}{\partial v}\right)_T + p\right]$

$$\tag{III.77}$$

Since $\partial^2 E/\partial T\,\partial v = \partial^2 E/\partial v\,\partial T$, this reduces to

$$\left(\frac{\partial E}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \tag{III.78}$$

From the first law it is easily seen that

$$\left(\frac{\partial E}{\partial T}\right)_v = \left(\frac{dQ}{dT}\right)_v = C_v$$

Making the proper substitutions in Eq. (III. 72) we obtain

$$dE = C_v\,dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv \tag{III.79}$$

Alternative Derivation.—The expressions for the two fundamental laws may be combined into the equation

$$T\,dS = dE + p\,dv \tag{III.80}$$

At constant temperature we may write this

$$T\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial E}{\partial v}\right)_T + p \tag{III.81}$$

Differentiating with respect to T at constant v,

$$T\left(\frac{\partial^2 S}{\partial v\,\partial T}\right) + \left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial^2 E}{\partial v\,\partial T}\right) + \left(\frac{\partial p}{\partial T}\right)_v \tag{III.82}$$

At constant volume,

$$dQ = dE$$
$$= C_v \, dT$$

and since, in general,

$$dQ = T \, dS$$

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v \tag{III.83}$$

or

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_v \tag{III.84}$$

Differentiating Eq. (III.84) with respect to volume at constant T,

$$\frac{\partial^2 E}{\partial T \, \partial v} = T \frac{\partial^2 S}{\partial T \, \partial v} \tag{III.85}$$

From Eqs. (III.82) and (III.85) $\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$ (III.86)

Now, since S is a property,

$$dS = \left(\frac{\partial S}{\partial T}\right)_v dT + \left(\frac{\partial S}{\partial v}\right)_T dv \tag{III.87}$$

From Eqs. (III.80) and (III.87),

$$dE = T\left(\frac{\partial S}{\partial T}\right)_v dT + T\left(\frac{\partial S}{\partial v}\right)_T dv - p \, dv$$

Substituting values for the differential coefficients from Eqs. (III.84) and (III.86),

$$dE = C_v \, dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p \right] dv \tag{III.79}$$

The corresponding equation for entropy is obtained at once from Eqs. (III.79) and (III.80).

$$dS = C_v \frac{dT}{T} + \left(\frac{\partial p}{\partial T}\right)_v dv \tag{III.88}$$

Equations with p and T as Independent Variables.—To derive the analogous equation in terms of the independent variables p and T, use may be made of the H function as follows: From the definition of H,

$$dH = dE + p \, dv + v \, dp \tag{III.7}$$

Combining with Eq. (III.80), $T \, dS = dH - v \, dp$ (III.89)

Dividing by dp at constant T,

$$T\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T - v \tag{III.90}$$

Now differentiate Eq. (III.90) with respect to T at constant p.

$$T \frac{\partial^2 S}{\partial p \, \partial T} + \left(\frac{\partial S}{\partial p}\right)_T = \frac{\partial^2 H}{\partial p \, \partial T} - \left(\frac{\partial v}{\partial T}\right)_p \qquad \text{(III.91)}$$

At constant p, $\qquad\qquad dQ = C_p \, dT = T \, dS$

or $\qquad\qquad\qquad \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \qquad\qquad\qquad \text{(III.92)}$

But $\qquad\qquad\qquad C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad\qquad\qquad \text{(III.9)}$

$$\therefore \; T \left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad\qquad \text{(III.93)}$$

and hence $\qquad\qquad T \frac{\partial^2 S}{\partial T \, \partial p} = \frac{\partial^2 H}{\partial T \, \partial p}$

Making this substitution in Eq. (III.91),

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \qquad\qquad \text{(III.94)}$$

Since S is a property,

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

Substituting from Eqs. (III.92) and (III.94), we obtain

$$dS = C_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_p dp \qquad\qquad \text{(III.95)}$$

From Eqs. (III.89) and (III.95) the analogous equation for H is obtained at once.

$$dH = C_p \, dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p \right] dp \qquad\qquad \text{(III.96)}$$

Constant H and S.—At constant H, one obtains from Eq. (III.96) the important equation

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{T(\partial v/\partial T)_p - v}{C_p} \qquad\qquad \text{(III.97)}$$

The coefficient $(\partial T/\partial p)_H$ is known as the Joule-Thomson coefficient and is commonly represented by μ.

At constant S, Eq. (III.95) can be transformed to

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{T(\partial v/\partial T)_p}{C_p} \qquad\qquad \text{(III.98)}$$

or $\qquad\qquad\qquad C_p = T \frac{(\partial v/\partial T)_p}{(\partial T/\partial p)_s} \qquad\qquad \text{(III.99)}$

Eq. (III.99) has been applied to measurement of specific heat at constant pressure.

In similar fashion, from Eq. (III.88) one obtains

$$C_v = -T \frac{(\partial p/\partial T)_v}{(\partial T/\partial v)_s} \tag{III.100}$$

Change of Independent Variable.—To change to the pair of variables p and v, use can be made of the equations between differential coefficients like the following:

$$\left(\frac{\partial S}{\partial v}\right)_p = \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial v}\right)_p \tag{III.101}$$

and
$$\left(\frac{\partial S}{\partial p}\right)_v = \left(\frac{\partial S}{\partial T}\right)_v \left(\frac{\partial T}{\partial p}\right)_v \tag{III.102}$$

These are based on Eq. (I.12). The proper substitutions will at once give

$$dS = \frac{C_p}{T}\left(\frac{\partial T}{\partial v}\right)_p dv + \frac{C_v}{T}\left(\frac{\partial T}{\partial p}\right)_v dp \tag{III.103}$$

and similarly for dE and dH.

It may be well to note at this point that the function E is chiefly useful when the independent variables are T and v and that the function H is chiefly useful when the independent variables are p and T. Having a differential coefficient such as $(\partial E/\partial T)_v$, it is sometimes desired to convert this to a similar one with another variable constant, for example, $(\partial E/\partial T)_p$. This may be accomplished by means of Eq. (I.13).

Specific-heat Relationships.—Some useful equations involving the two common specific heats are readily derived as follows: Applying

$$\frac{\partial^2 E}{\partial v\,\partial T} = \frac{\partial^2 E}{\partial T\,\partial v}$$

to Eq. (III.79), one obtains

$$\left(\frac{\partial C_v}{\partial v}\right)_T = \left\{\frac{\partial[T(\partial p/\partial T)_v - p]}{\partial T}\right\}_v = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v \tag{III.104}$$

In similar fashion, apply the criterion

$$\frac{\partial^2 H}{\partial p\,\partial T} = \frac{\partial^2 H}{\partial T\,\partial p}$$

to Eq. (III.96) and obtain

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p \tag{III.105}$$

Now, from Eqs. (III.88) and (III.95),

$$dQ = T\,dS = C_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_v dv \tag{III.106}$$

$$T\,dS = C_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_p dp \tag{III.107}$$

and since $v = \phi(p,T)$,

$$dv = \left(\frac{\partial v}{\partial p}\right)_T dp + \left(\frac{\partial v}{\partial T}\right)_p dT \tag{III.108}$$

and

$$\left(\frac{\partial p}{\partial T}\right)_v = -\frac{(\partial v/\partial T)_p}{(\partial v/\partial p)_T} \tag{III.109}$$

Substituting Eq. (III.108) in Eq. (III.106),

$$dQ = \left[C_v + T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p\right]dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial p}\right)_T\right]dp \tag{III.110}$$

and, using Eq. (III.109),

$$dQ = \left[C_v + T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p\right]dT - T\left(\frac{\partial v}{\partial T}\right)_p dp \tag{III.111}$$

Upon comparing Eqs. (III.111) and (III.107), it is evident that

$$C_p = C_v + T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p \tag{III.112}$$

Utilizing Eq. (III.109), we can readily put this in the following form:

$$C_p - C_v = -T\left(\frac{\partial v}{\partial T}\right)_p^2\left(\frac{\partial p}{\partial v}\right)_T \tag{III.113}$$

Eqs. (III.112) and (III.113) can be used for the calculation of C_p from C_v, or vice versa, for any substance once its pvT behavior is known.

From Eqs. (III.99) and (III.100) and the equations

$$\left(\frac{\partial p}{\partial T}\right)_S\left(\frac{\partial T}{\partial v}\right)_S = \left(\frac{\partial p}{\partial v}\right)_S$$

and

$$\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial T}{\partial v}\right)_p = -\left(\frac{\partial p}{\partial v}\right)_T$$

which follow at once from Eqs. (I.12) and (I.16), one can get

$$\frac{C_p}{C_v} = \frac{(\partial p/\partial v)_S}{(\partial p/\partial v)_T} = \frac{\kappa_S}{\kappa_T} \tag{III.114}$$

where

$$\kappa_S = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_S$$

and

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$$

These are the adiabatic and isothermal compressibilities, respectively.

Equations for A and F.—Equations relating A and F to other properties are readily derived as follows:

$$A = E - TS \qquad \text{by definition}$$

Differentiating, $\qquad dA = dE - T\,dS - S\,dT \qquad \text{(III.115)}$

But $\qquad\qquad\quad dE - T\,dS = -p\,dv \qquad\qquad \text{(III.80)}$

$$\therefore dA = -p\,dv - S\,dT \qquad \text{(III.116)}$$

and $\qquad\qquad \left(\dfrac{\partial A}{\partial v}\right)_T = -p \qquad\qquad \text{(III.117)}$

$$\left(\dfrac{\partial A}{\partial T}\right)_v = -S \qquad\qquad \text{(III.118)}$$

Equations for A in terms of the other pairs of variables are not so simple as these and are of no particular use. In other words, the A function is useful only when the independent variables are T and v.

Similarly, $\qquad F = E - TS + pv, \qquad\qquad \text{by definition}$

$$dF = dE - T\,dS - S\,dT + p\,dv + v\,dp$$

but $\qquad\qquad\quad dE - T\,dS + p\,dv = 0$

$$\therefore dF = -S\,dT + v\,dp \qquad\qquad \text{(III.119)}$$

and $\qquad\qquad \left(\dfrac{\partial F}{\partial T}\right)_p = -S \qquad\qquad \text{(III.120)}$

$$\left(\dfrac{\partial F}{\partial p}\right)_T = v \qquad\qquad \text{(III.121)}$$

The function F is always the one to use when the independent variables are p and T.

Derivations Using A and F.—It is interesting to see how some of the derivations of E, H, and S equations previously made could be simplified by the use of functions A and F. We shall digress for a moment to demonstrate this.

Let us start with Eqs. (III.116) and (III.119). It follows at once from these equations and Eq. (I.19) that

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \qquad\qquad \text{(III.86)}$$

and $\qquad\qquad \left(\dfrac{\partial S}{\partial p}\right)_T = -\left(\dfrac{\partial v}{\partial T}\right)_p \qquad\qquad \text{(III.94)}$

Now $\qquad\qquad T\,dS = dQ = C_v\,dT \qquad \text{(at constant volume)}$

$$= C_p\,dT \qquad \text{(at constant pressure)}$$

or $\qquad\qquad\quad \left(\dfrac{\partial S}{\partial T}\right)_v = \dfrac{C_v}{T}$

and $\qquad\qquad \left(\dfrac{\partial S}{\partial T}\right)_p = \dfrac{C_p}{T}$

From these it follows at once that

$$dS = \frac{C_v}{T} dT + \left(\frac{\partial p}{\partial T}\right)_v dv \tag{III.88}$$

$$dS = \frac{C_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp \tag{III.95}$$

Then, from $T \, dS = dE + p \, dv$ (III.80)

and $T \, dS = dH - v \, dp$ (III.89)

one can get at once the corresponding E and H equations.

Free Energy as a Function of Temperature.—From Eq. (III.120) and the fact that

$$F = H - TS \tag{III.122}$$

one obtains

$$\left(\frac{\partial F}{\partial T}\right)_p = \frac{F - H}{T} \tag{III.123}$$

Then $T \, dF - F \, dT = -H \, dT$ (at constant pressure)

and $\dfrac{T \, dF - F \, dT}{T^2} = -\dfrac{H \, dT}{T^2}$

or

$$\frac{\partial (F/T)}{\partial T} = -\frac{H}{T^2} \tag{III.124}$$

Integrating,

$$\frac{F}{T} = -\int H \frac{dT}{T^2} + I \tag{III.125}$$

where I is an integration constant.

H is readily expressed as a function of T through the specific heats, and integration then yields a very important equation relating free energy and temperature. Thus,

$$\left(\frac{\partial H}{\partial T}\right) = C_p \tag{III.9}$$

or $H = H_0 + \int C_p \, dT$

where H_0 is an integration constant. It would, of course, be the value of H at absolute zero if the equation were integrated with the aid of C_p data valid to $T = 0$.

Assume $C_p = \alpha + \beta T + \gamma T^2$ (III.126)

Then $H = H_0 + \alpha T + \frac{1}{2}\beta T^2 + \frac{1}{3}\gamma T^3$ (III.127)

Substitute Eq. (III.127) in Eq. (III.125), and integrate.

$$\frac{F}{T} = \frac{H_0}{T} - \alpha \ln T - \frac{1}{2}\beta T - \frac{1}{6}\gamma T^2 + I$$

or $F = H_0 - \alpha T \ln T - \frac{1}{2}\beta T^2 - \frac{1}{6}\gamma T^3 + IT$ (III.128)

Also, $F = H - \alpha T \ln T - \beta T^2 - \frac{1}{2}\gamma T^3 + (I - \alpha)T$ (III.129)

As it stands, this equation applies only to a homogeneous single-component system, but it will later be extended to more complex systems. Note that it is for the change of F with T *at constant pressure*.

F as a function of temperature is also obtainable from the relation

$$F = H - TS \qquad \text{(III.122)}$$

by expressing S and H as functions of T at constant p. Since

$$dS = C_p \frac{dT}{T}$$

$$S = \int C_p \, d \ln T + S_0 \qquad \text{(III.130)}$$

S_0 would be the entropy at $T = 0$ if the equation for C_p were valid to $T = 0$.

Utilizing Eq. (III.126), $\quad S = \displaystyle\int (\alpha + \beta T + \gamma T^2) \frac{dT}{T} + S_0$

$$= \alpha \ln T + \beta T + \tfrac{1}{2}\gamma T^2 + S_0 \qquad \text{(III.131)}$$

Substituting (III.127) and (III.131) in Eq. (III.122),

$$F = H_0 - \alpha T \ln T - \tfrac{1}{2}\beta T^2 - \tfrac{1}{6}\gamma T^3 + (\alpha - S_0)T \qquad \text{(III.132)}$$

From this method of derivation one sees more clearly that the constant of integration I is directly related to entropy and would be determinable if specific heats were known down to $T = 0$ and if the entropy at absolute zero were known.

Before leaving the discussion of these two functions it may be of interest to note that the enthalpy H may be calculated from a knowledge of F as a function of p and T. This follows from (III.124), which may also be put in the form

$$\frac{\partial (F/T)_p}{\partial (1/T)_p} = H \qquad \text{(III.133)}$$

Similarly, E may be calculated from A as a function of v and T by the relation

$$\frac{\partial (A/T)_v}{\partial (1/T)_v} = E \qquad \text{(III.134)}$$

A AND F AS CRITERIA OF EQUILIBRIUM

Whenever a tendency for spontaneous change exists, work can be obtained from the process if a suitable mechanism is provided. The maximum possible work is obtained when the process takes place with balanced forces, *i.e.*, reversibly. For a constant-temperature process, the maximum work is measured by a *decrease* in the function A. Similarly, for a process operating both at constant temperature and constant pressure, the maximum *useful* work is measured by a *decrease* in the function F. In other words, A and F always decrease in any spontaneous

process, and for this reason they can be used as criteria to tell whether or not an imagined process will or will not take place.

For example, consider some system in an initial state 1, and suppose that its free energy F is known. Assume that we wish to know whether a change to another state 2 will take place, of itself, under conditions of constant temperature and pressure or whether energy would have to be applied to make it go. In principle, this is one of the most common types of question that arise in dealing with chemical systems. If we know the value of the free energy in state 2, the answer is very simple. The contemplated change will take place if F_2 is $< F_1$, in other words, if there is a decrease in free energy.[1] If $F_2 > F_1$, the change cannot possibly occur spontaneously. Thus A and F are criteria of the direction of spontaneous change. For this reason, they are sometimes called "potential functions," a "potential" being a quantity used in theoretical mechanics whose value always decreases in the direction of a spontaneous change.

Equation (III.56) without the inequality applies quite generally to a system at equilibrium, and the same is true of the derived equations (III.116) and (III.119). From Eq. (III.116) at constant v and T, we have

$$dA = 0 \qquad \text{(III.135)}$$

and, from Eq. (III.119) at constant p and T,

$$dF = 0 \qquad \text{(III.136)}$$

These two equations are commonly stated to be important criteria of equilibrium. Actually, when applied to one-component single-phase systems they have no meaning because no change is possible in such a system when two of the state variables are fixed. However, when one considers more complex systems, other changes, such as mass transfer between phases or chemical reactions, are possible; these equations can then be applied to derive some important equilibrium relations. This will be demonstrated in the next chapter.

FUGACITY AND ACTIVITY

These special functions were introduced by G. N. Lewis in 1901,[2] in order to simplify the treatment of cases in which the ideal-gas and ideal-

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[1] It is not quite correct, from a practical standpoint, to say that the change *will* take place. It will have a *tendency* to take place; but certain resistance effects analogous to static mechanical friction may so decrease the rate of change that, for all practical purposes, it does not take place. Furthermore, it is to be noted that we have purposely departed from a rigorous mathematical treatment in order to simplify the argument. Strictly, one should deal only with differential and not with finite changes in such a treatment.

[2] LEWIS, G. N., *Proc. Am. Acad. Arts Sci.*, **37**, 49 (1901).

solution laws do not apply. The functions are chiefly useful in dealing with solutions rather than single-component systems, but we shall define them here for the more simple case and then later in Chap. IV generalize the definitions to include the case of more than one component.

Definition of Fugacity.—From Eq. (III.119) we may write, at constant temperature,

$$dF = v \, dp \tag{III.137}$$

In the special case where the substance is an ideal gas, $v = RT/p$.

$$\therefore \ dF = RT \, d \ln p \tag{III.138}$$

In order to preserve the form of this equation for other cases in which the system is not an ideal gas, Lewis defines a special function by the equation

$$dF = RT \, d \ln f = v \, dp \tag{III.139}$$

where f is the fugacity of the system.

Integrating Eq. (III.139) at constant temperature between two states at different pressures,

$$F - F^\circ = RT \ln \frac{f}{f^\circ} = \int_{p^\circ}^{p} v \, dp \tag{III.140}$$

where p° is the pressure in an arbitrary standard state.

Equation (III.140) merely defines a ratio of fugacities in two isothermal states and does not suffice to assign any absolute numerical value to fugacity. Comparison of Eqs. (III.138) and (III.139) shows that, for an ideal gas, fugacity is proportional to the pressure. Now, from a purely theoretical standpoint, any substance whether solid, liquid, or gaseous can be brought to the state of an ideal gas if we decrease, at constant temperature, the pressure upon it. All liquids, and even solids, will eventually vaporize and all gases will tend to approach the ideal state as the pressure is lowered. This is confirmed by the experimental observation of the behavior of gaseous systems as the pressure is lowered. Also, most equations of state that relate the pvT properties of gases reduce to the simple ideal-gas form ($pv = RT$) at the limit when $p = 0$ or $v = \infty$.

It is convenient to complete the definition of fugacity by making it numerically equal to the pressure when the substance is in the state of an ideal gas. Let the state represented by p° and f° be such a state, and therefore $p^\circ = f^\circ$.

For all practical purposes, p° can be taken as some definite low pressure such as 1 atm. or preferably 0.1 atm. where the deviation from the ideal-gas law is small for most systems and probably within the experimental error. Actually, the common practice is to take p° equal to

1 atm. This leads to a certain amount of confusion because it will represent a purely hypothetical state in many cases. For example, one may be dealing with a gaseous reaction at elevated temperature involving some condensable vapor—water vapor, for instance. Some of the fundamental data will be available at 25°C., and so it will be necessary to consider standard states at this temperature, at which water vapor does not exist as a gas at 1 atm. pressure. It is simpler to extrapolate the properties into an unstable region than to change the standard state to a lower pressure. Any small error caused by such an extrapolation is more than offset by the greater convenience in a practical case. To be mathematically rigorous, one should go to the limit where p approaches zero. As Tunell[1] points out in an exhaustive and rigorous study of the definition of fugacity, Eq. (III.140) does not define the fugacity in all states along a given isotherm because, at the limit where p approaches zero, $F°$ approaches $-\infty$. There appears to be no rigorous, mathematical way to prove the equation

$$\lim_{p \to 0} \frac{f}{p} = 1 \qquad \text{(III.141)}$$

Tunell suggests the following equation as a more satisfactory definition of fugacity:

$$RT \ln f = RT \ln p - \int_0^p \alpha \, dp \qquad \text{(III.142)}$$

where α is the function $(RT/p) - v$.

This definition does not lead to indeterminate values at the limit if one accepts the hypothesis that α approaches a constant finite value at $p = 0$.* This hypothesis is based on actual observation of the experimental behavior of α as a function of pressure (see Chap. V).

The definition of Tunell makes no change whatever in the numerical evaluation of fugacity because Eq. (III.142) has been the one used for its evaluation by Lewis and Randall and all subsequent workers. Furthermore, both Tunell's and Lewis's definitions lead to exactly the same expression for calculating fugacity from equations of state.

Equation (III.140) can also be written

$$RT \ln f - RT \ln f° = \int v \, dp - RT \ln p°$$

and since $f° = p°$,

$$\ln f = \frac{1}{RT} \int v \, dp \qquad \text{(III.143)}$$

[1] TUNELL, G., *J. Phys. Chem.*, **35**, 2885–2913 (1931).
* It may seem contradictory that, whereas $pv = RT$ as $p \to 0$, $(RT/p) - v$ does not approach zero. That such is the case, however, is best demonstrated by means of an equation of state, as will be shown in Chap. V.

Effect of Pressure and Temperature on Fugacity.—Change of fugacity with the pressure is given by the following equation, rearranged from (III.139):

$$\left(\frac{\partial \ln f}{\partial p}\right)_T = \frac{v}{RT} \tag{III.144}$$

Its change with temperature may be derived as follows:

Differentiation of the first part of Eq. (III.140) at constant pressure leads to

$$\left(\frac{\partial F}{\partial T}\right)_p - \left(\frac{\partial F^\circ}{\partial T}\right)_{p^\circ} = R \ln \frac{f}{f^\circ} + RT\left[\left(\frac{\partial \ln f}{\partial T}\right)_p - \left(\frac{\partial \ln f^\circ}{\partial T}\right)_{p^\circ}\right] \tag{III.145}$$

Making the following substitutions in Eq. (III.145),

$$\left(\frac{\partial F}{\partial T}\right)_p = \frac{F}{T} - \frac{H}{T} \tag{III.123}$$

$$R \ln \frac{f}{f^\circ} = \frac{F}{T} - \frac{F^\circ}{T} \qquad \text{[from Eq. (III.140)]}$$

and

$$\left(\frac{\partial \ln f^\circ}{\partial T}\right)_{p^\circ} = 0$$

(since $f^\circ = p^\circ$ from the definition of fugacity), we obtain

$$\left(\frac{\partial \ln f}{\partial T}\right)_p = \frac{H^\circ - H}{RT^2} \tag{III.146}$$

$H^\circ - H$ is the difference between the enthalpy of the substance in the initial state of low pressure (p°) and that in the given state, both at the same temperature.

Definition of Activity.—In many cases it will be more convenient to deal simply with the ratio of the fugacity in the given state to that in some arbitrary standard state at the same temperature. This ratio was called the "activity" by G. N. Lewis, and it is represented by the symbol a. Thus, by definition,

$$a = \frac{f}{f^\circ}$$

and hence, from Eq. (III.140),

$$F - F^\circ = RT \ln a \tag{III.147}$$

The activity may be defined directly on the basis of this equation instead of referring it to fugacity.

In order to obtain a numerical value for the activity, the standard state must be specified. Actually, the activity function is used only in treating solutions; and since we are concerned with pure substances in this chapter, further discussion of this function will be deferred until later.

APPLICATION TO IDEAL GASES

Our primary objective in this chapter was the development of various general relationships that could later be applied to specific problems, but it seems desirable to conclude our discussion by considering the application of some of the equations to the simplest possible case, *viz.*, that of the ideal gas.

For present purposes the ideal gas will be defined as a gas that obeys the following equation of state:

$$pv = RT \tag{III.148}$$

By differentiation of Eq. (III.148), the following coefficients are obtained:

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v} \tag{III.149}$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} \tag{III.150}$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0 \tag{III.151}$$

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = 0 \tag{III.152}$$

Upon utilizing these equations, which, it should be noted, apply only to the ideal gas, Eqs. (III.79), (III.88), (III.95), (III.96), (III.104), (III.105), (III.112), (III.116), and (III.119) are transformed to the following equations, respectively:

$$dE = C_v \, dT \tag{III.153}$$

$$dS = C_v \frac{dT}{T} + R \frac{dv}{v} \tag{III.154}$$

$$dS = C_p \frac{dT}{T} - R \frac{dp}{p} \tag{III.155}$$

$$dH = C_p \, dT \tag{III.156}$$

$$\left(\frac{\partial C_v}{\partial v}\right)_T = 0 \tag{III.157}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = 0 \tag{III.158}$$

$$C_p - C_v = R \tag{III.159}[1]$$

$$dA = -RT \frac{dv}{v} - S \, dT \tag{III.160}$$

$$dF = RT \frac{dp}{p} - S \, dT \tag{III.161}$$

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[1] Note that this applies only to molal heat capacity. The equivalent equation for specific heats is $c_p - c_v = R/M$ where M = molecular weight.

From these equations we can draw the following important quali-tative conclusions: (1) the energy, (2) the enthalpy, (3) the specific heat at constant volume, and (4) the specific heat at constant pressure of the ideal gas are all functions of the temperature only. Change in pressure or volume at constant temperature will not alter their values.

Illustration 11.—Calculate the energy, enthalpy, entropy, molal heat capacity at constant volume, molal heat capacity at constant pressure, and free energy of 1 lb.-mole of nitrogen at 500°C. and 100 atm. absolute pressure, assuming it to be an ideal gas and given the following:

1. Molal heat capacity at 1 atm. as a function of temperature is given by the equation

$$C_p = 6.50 + 0.001T$$

where T is in degrees Kelvin and C_p in calories per gram-mole per degree centigrade.

2. Enthalpy is arbitrarily taken to be zero at 0°C. and 1 atm. absolute pressure.
3. Entropy of nitrogen at 25°C. and 1 atm. abs. = 45.8 cal. per °C. per g.-mole.

$$C_p \text{ at } 500°C. \text{ and } 1 \text{ atm.} = 6.50 + 0.001 \times 773 = 7.273$$

By Eq. (III.159),

$$C_v \text{ at the same state} = C_p - R = 7.273 - 1.987 = 5.286$$

By Eqs. (III.157) and (III.158), C_p and C_v are independent of the pressure and so the above values also apply to 100 atm. pressure.
By Eq. (III.156),

$$H = H_0 + \int_{T_0}^{T} C_p \, dT$$
$$= 0 + \int_{273}^{773} (6.50 + 0.001T) \, dT = 3{,}512 \text{ c.h.u./lb.-mole (or g.-cal./g-mole)}$$

This is the enthalpy of N_2 at 500°C. and 1 atm.; but since we have seen that the enthalpy is independent of pressure, so it is also the enthalpy at 500°C. and 100 atm.

From Eq. (III.153), $\quad E = E_0 + \int_{T_0}^{T} C_v \, dT = E_0 + \int_{T_0}^{T} (C_p - R) \, dT$

We could use this equation, but it is simpler to calculate E from the relation

$$E = H - pv$$
$$= H - RT$$
$$= 3{,}512 - 1.987 \times 773 = 1{,}974 \text{ c.h.u.}$$

E is also independent of the pressure (or the volume) at constant temperature. By Eq. (III.154),

$$S = S_0 + \int_{T_0}^{T} C_p \frac{dT}{T} - R \int_{p_0}^{p} \frac{dp}{p} \tag{1}$$
$$= 45.8 + \int_{298}^{773} \left(6.50 \frac{dT}{T} + 0.001 \, dT \right) - 1.987 \ln 100$$
$$= 43.3$$

By Eq. (III.161), $\qquad F - F_0 = RT \int_{p_0}^{p} \frac{dp}{p} - \int_{T_0}^{T} S \, dT$

Integrating first along a constant pressure path $p_0 = 1$ and then at the constant temperature T, and using the relation

$$S = S_0 + \int_{T_0}^{T} C_p d \ln T \quad \text{[from Eq. (1) at constant } p]$$

we have $F = F_0 + RT \ln \frac{p}{p_0} - S_0 \int_{T_0}^{T} dT - \int_{T_0}^{T} \left(\int_{T_0}^{T} C_p \, d \ln T \right) dT$ (2)

Instead of using Eq. (2) to calculate F, it is much simpler in this case to use directly the equation defining F, *viz.*,

$$F = H - TS$$
$$= 3,512 - 773 \times 43.3 = -29,990$$

This value has no absolute significance because it is based on a purely arbitrary value for H_0.

It is important to notice that, whereas values of ΔH or ΔE or ΔS, differences in the values of these functions between any two states, *are entirely independent of the value chosen at the initial state, this is not true of* ΔF.   From Eq. (2) it is evident that the value of ΔF will depend on the value of S_0; and since there must be a definite value of ΔF for a given state change, it is clear that ΔF can be calculated from thermal data only if entropy can be assigned an absolute value.

CHAPTER IV

GENERAL EQUATIONS OF EQUILIBRIUM

In the preceding chapter we developed a number of important equations for the case of a relatively simple system—*viz.*, a single component in a single phase, subjected only to a uniform fluid pressure. In this chapter we shall extend the treatment to include systems of more than one component in a given phase (solutions) and systems of more than one phase. Furthermore, it will be desirable to show how the equations can also be extended to cases where other forces are involved, more especially electrical and magnetic forces. We shall, however, restrict the treatment to so-called "closed systems," or systems whose total mass remains a constant. Furthermore, we shall rule out liquid solutions in which electrolytic dissociation occurs, as these require special treatment.

It is our intention to show that many types of equilibria, often treated in unrelated fashion, are really closely related in that they may all be derived from a few general equations, which, in turn, are based directly on the fundamental concepts of thermodynamics as expressed by the various functions. Although the derivation of the general equations may seem more difficult and complex to the beginner than the less rigorous derivation of special equations, nevertheless it is believed that this method which we have adopted is really the simpler one in the long run. The general equations act as a unifying thread for a mass of otherwise unconnected phenomena, and the special equations fall out of the general ones in an almost automatic way when the specific conditions are put into them.

We shall admit at the start that the general equations themselves cannot usually be applied to any specific problems. This is due to the fact that the integrated forms would be quite complex and also that the data necessary for their integration are seldom available. Nevertheless, the general equations are valuable as the starting point for special relationships that have proved useful. By way of example, one might cite the following special relations that come readily from the general equations:

1) Clausius-Clapeyron equation.
2) Raoult's law.
3. Henry's law.
4. Duhem equation.

5. Freezing-point lowering in a dilute solution.

6. Phase rule.

7. Mass-action law for chemical equilibrium.

This chapter will be almost entirely mathematical and without the leaven of numerical illustrations. It is not intended that it should be mastered *in toto* by the student; rather, it is to be regarded primarily as a storehouse for a large number of relations that may prove useful in the solution of problems. Many of the equations, but by no means all, will be utilized in subsequent chapters; at the time of application it would be desirable to refer to this chapter for the derivation.

GENERAL EQUATIONS FOR ANY EXTENSIVE PROPERTY

Let **G** represent the total value of any extensive property, such as volume, enthalpy, or free energy, of a homogeneous system or solution of N components. In order to focus attention wholly on the change in **G** as a result of changes in the amounts of the various components of the solution, we shall assume that other independent variables such as pressure and temperature are fixed. Thus we may write,

$$\mathbf{G} = \phi(N_A, N_B, \cdots, N_N) \tag{IV.1}$$

Differentiating Eq. (IV.1),

$$d\mathbf{G} = \frac{\partial \mathbf{G}}{\partial N_A} dN_A + \frac{\partial \mathbf{G}}{\partial N_B} dN_B \cdots + \frac{\partial \mathbf{G}}{\partial N_N} dN_N \tag{IV.2}$$

It is understood that each one of the partial derivatives is at constant p and T (or whatever the particular external variables are) and at constant each of the other molal masses. We could, of course, write the same equation in terms of ordinary mass, but in general it will be simpler to deal with molal mass. We must recognize, however, that this involves the assignment of a definite and constant (though possibly arbitrary) molecular weight to each component in the solution. This may cause some ambiguity in a few cases but on the whole it proves to be the simplest procedure.[1]

The quantities $\partial \mathbf{G}/\partial N_i$ are commonly called "partial molal quantities" and are conveniently represented by the symbol $\bar{G}_i$. Thus we may write (IV.2) in the form

$$d\mathbf{G} = \bar{G}_A dN_A + \bar{G}_B dN_B + \cdots + \bar{G}_N dN_N \tag{IV.3}$$

The nature of an extensive property is such that if one increases all the masses of the solution in the same proportion, *i.e.*, does not change the composition, or *relative* masses, the value of the property increases in

[1] Most of the equations in this section would be identical whether one uses molal property and mole fraction or the specific property based on unit mass and mass fraction, but the actual treatment will be in terms of the mole units.

that proportion. In other words, two pound-moles of any solution will
have just double the volume or the enthalpy of one pound-mole provided
that the pressure, temperature, and composition have not changed. If
we doubled the total mass at constant p and T but did not keep the masses
of the individual components in the same ratio, then the value of **G**
would not be doubled.

These simple and practically obvious facts can be stated more
elegantly by saying that **G** is a homogeneous function of the masses to
the first degree. From a mathematical proposition, known as Euler's
theorem, it follows that the coefficients $\partial G/\partial N_i$ are functions of the
masses to the zero degree, or, in other words, are independent of the
masses themselves and depend only on mass ratios, or composition.

Integrating Eq. (IV.3) at constant composition,

$$\mathbf{G} = \bar{G}_A N_A + \bar{G}_B N_B \cdots + \bar{G}_N N_N \qquad (IV.4)$$

The integration constant is zero as may readily be seen by considering
the physical picture of the integration process. It simply amounts to
adding together small increments of the *given* solution to produce a finite
amount of the same solution.

Equation (IV.4) may now be differentiated without regard to the
special restriction of constant composition, giving

$$d\mathbf{G} = \bar{G}_A \, dN_A + N_A \, d\bar{G}_A + \bar{G}_B \, dN_B + N_B \, d\bar{G}_B + \cdots$$
$$+ \bar{G}_N \, dN_N + N_N d\bar{G}_N \quad (IV.5)$$

Comparing Eqs. (IV.3) and (IV.5),

$$N_A \, d\bar{G}_A + N_B \, d\bar{G}_B + \cdots + N_N \, d\bar{G}_N = 0 \qquad (IV.6)$$

Instead of working with the value of an extensive property based on
the total mass, it will be more convenient in most of our discussion to deal
with the various properties on a unit basis, and then Eqs. (IV.2), (IV.4),
and (IV.6) become, respectively,

$$dG = \bar{G}_A \, dx_A + \bar{G}_B \, dx_B + \cdots + \bar{G}_N \, dx_N \qquad (IV.7)$$
$$G = x_A \bar{G}_A + x_B \bar{G}_B + \cdots + x_N \bar{G}_N \qquad (IV.8)$$
and $\qquad\qquad x_A \, d\bar{G}_A + x_B \, d\bar{G}_B + \cdots + x_N \, d\bar{G}_N = 0 \qquad (IV.9)$

where the x's are the mole fractions of the various components.[1] From
the fact that

$$x_A + x_B + \cdots + x_N = 1 \qquad (IV.10)$$

we obtain

$$dx_N = -dx_A - dx_B - \cdots - dx_{N-1} \qquad (IV.11)$$

[1] It should be noted that, since the x's are not all independent, $\bar{G}_i$ is not equal to
$\partial G/\partial x_i$.

Eliminating dx_N from Eq. (IV.7) by means of (IV.11),

$$dG = (\bar{G}_A - \bar{G}_N)\, dx_A + (\bar{G}_B - \bar{G}_N)\, dx_B + \cdots + (\bar{G}_{N-1} - \bar{G}_N)\, dx_{N-1} \tag{IV.12}$$

Since all the x's are now independent variables, we can write

$$\left(\frac{\partial G}{\partial x_i}\right)_{x_A, x_B, \cdots} = \bar{G}_i - \bar{G}_N \tag{IV.13}$$

the subscript i referring to any component.

From Eqs. (IV.8) and (IV.10),

$$G = (\bar{G}_A - \bar{G}_N)x_A + (\bar{G}_B - \bar{G}_N)x_B + \cdots + (\bar{G}_{N-1} - \bar{G}_N)x_{N-1} + \bar{G}_N \tag{IV.14}$$

or

$$\bar{G}_N = G - (\bar{G}_A - \bar{G}_N)x_A - (\bar{G}_B - \bar{G}_N)x_B - \cdots - (\bar{G}_{N-1} - \bar{G}_N)x_{N-1} \tag{IV.15}$$

Substituting Eq. (IV.13) in Eq. (IV.15),

$$\bar{G}_N = G - x_A \frac{\partial G}{\partial x_A} - x_B \frac{\partial G}{\partial x_B} - \cdots - x_{N-1} \frac{\partial G}{\partial x_{N-1}} \tag{IV.16}$$

and, comparing with (IV.13),

$$\bar{G}_i = G + \frac{\partial G}{\partial x_i} - x_A \frac{\partial G}{\partial x_A} - x_B \frac{\partial G}{\partial x_B} - \cdots - x_{N-1} \frac{\partial G}{\partial x_{N-1}} \tag{IV.17}$$

In all this section we have been heading toward these last two equations. Equation (IV.17) relates the partial molal property of any component, except the one whose mole fraction has been eliminated, to the molal property and the composition of the solution. Equation (IV.16) does the same for the component N whose mole fraction was eliminated through the use of Eq. (IV.10).

Special Case of Binary Solution.—To obtain a somewhat more concrete idea of the partial molal quantities, let us consider very briefly the special case of a binary solution of mole fractions x and $1 - x$ and take the volume as the property with the pressure and temperature fixed. Equations (IV.16) and (IV.17) become, respectively,

$$\bar{v}_B = v - x \frac{\partial v}{\partial x} \tag{IV.18}$$

and

$$\bar{v}_A = v + (1 - x) \frac{\partial v}{\partial x} \tag{IV.19}$$

The values of the partial molal volumes could readily be obtained from values of the molal volume of the solution as a function of the mole fraction, either by algebraic or by graphical methods. The **graphical**

method will be illustrated in Chap. IX for the special case of the differential heat of solution, which is a partial molal enthalpy.

Typical Equation for a Partial Molal Property.—Many of the equations derived in the preceding chapter relating the extensive properties of a single component can be readily extended to the corresponding partial molal quantities. Consider, for example, the following equation:

$$\left(\frac{\partial H}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$$

which follows at once from Eq. (III.96). This equation applies equally well to molal properties or to total properties of a homogeneous system. Differentiate the equation in terms of total properties with respect to N_i, the number of moles of any component, at constant p and T, and obtain

$$\frac{\partial^2 H}{\partial p\,\partial N_i} = \frac{\partial V}{\partial N_i} - T\,\frac{\partial^2 V}{\partial T\,\partial N_i}$$

This can be written,

$$\left[\frac{\partial(\partial H/\partial N_i)_{p,T,N_A,N_B,\cdots}}{\partial p}\right]_{T,x,\cdots}$$
$$= \left(\frac{\partial V}{\partial N_i}\right)_{p,T,N_A,N_B,\cdots} - T\left[\frac{\partial(\partial V/\partial N_i)_{p,T,N_A,N_B,\cdots}}{\partial T}\right]_{p,x,\cdots}$$

or
$$\left(\frac{\partial \bar{H}_i}{\partial p}\right)_{T,x,\cdots} = \bar{v}_i - T\left(\frac{\partial \bar{v}_i}{\partial T}\right)_{p,x,\cdots} \qquad \text{(IV.20)}$$

As we have seen, the partial molal quantities are functions not of the individual masses but of the composition. Consequently, a partial derivative of a partial molal quantity with respect to pressure or temperature must be at *constant composition*. The notation $x, \cdots$ represents $(N - 1)$ composition variables.

EQUILIBRIUM EQUATIONS FOR ANY NUMBER OF COMPONENTS AND PHASES

The Chemical Potentials.—The fundamental equation of equilibrium for a single component homogeneous system in which only mechanical forces are acting is given by the following equation,

$$dE = T\,dS - p\,dv \qquad \text{(III.80)}$$

or in the equivalent form, using the free-energy function,

$$dF = -S\,dT + v\,dp \qquad \text{(III.119)}$$

These equations apply equally well to any homogeneous solution of fixed composition. Consider a solution containing $N_A, N_B, \ldots, N_N$

moles of components A, B, . . . , N, respectively. The number of moles of any component can be varied independently of any other (definition of component), and such variations will cause a change in the energy or the free energy of the mixture or solution. Since these changes are independent, we may write

$$dE = T\,dS - p\,dV + \frac{\partial E}{\partial N_A}\,dN_A + \frac{\partial E}{\partial N_B}\,dN_B + \cdots + \frac{\partial E}{\partial N_N}\,dN_N \quad (\text{IV.21})$$

where the partial derivatives are at constant S, V and each of the other N's. Likewise, we may write

$$dF = -S\,dT + V\,dp + \frac{\partial F}{\partial N_A}\,dN_A + \frac{\partial F}{\partial N_B}\,dN_B + \cdots + \frac{\partial F}{\partial N_N}\,dN_N \quad (\text{IV.22})$$

Now since, by definition,

$$F = E - TS + pV,$$

then $$dE - T\,dS + p\,dV = dF + S\,dT - V\,dp$$

and the coefficients of the dN terms in (IV.21) and (IV.22) are identical, or

$$\left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_A,\,\cdots} = \left(\frac{\partial F}{\partial N_i}\right)_{p,T,N_A,\,\cdots} \quad (\text{IV.23})$$

Since E and F are extensive properties, these coefficients are the quantities we have already called "partial molal quantities." These particular ones have a special significance in connection with equilibrium states and were called "chemical potentials" by Gibbs,[1] who was the first to realize their significance. We shall adopt this nomenclature and represent the chemical potentials by the symbol μ. A chemical potential can be defined in four different ways, depending on the choice of independent variables; for example,

$$\mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_A,\,\cdots} = \left(\frac{\partial H}{\partial N_i}\right)_{S,p,N_A,\,\cdots} = \left(\frac{\partial A}{\partial N_i}\right)_{V,T,N_A,\,\cdots}$$
$$= \left(\frac{\partial F}{\partial N_i}\right)_{p,T,N_A,\,\cdots}$$

From our discussion of partial molal quantities it is evident that the chemical potentials are intensive properties like pressure and temperature, depending on the composition of the solution, but not on the total mass. The chemical potential of any component in a phase is the rate at which the *total* free energy (as distinct from the molal value) of that phase changes as one changes the amount of that particular component, keeping the pressure, temperature, and amounts of all the other components of

[1] GIBBS, J. W., *Trans. Connecticut Acad.*, **3**, 108–248, 343–524 (1875–1878).

the phase the same. Similarly, it is the rate at which the total enthalpy of the phase changes when the amount of a particular component is varied, maintaining the entropy, pressure, and amounts of all the other components invariant. Since the pressure and temperature are the two independent variables that are commonly chosen in any actual problem, the partial molal free energy is used practically to the exclusion of the other chemical potentials.

Criterion of Equilibrium.—In his celebrated paper On the Equilibrium of Heterogeneous Substances, Josiah Willard Gibbs develops as a general criterion of equilibrium the relation

$$d\mathbf{E} = 0 \quad \text{at constant } S \text{ and } V \quad \text{(IV.24)}$$

The student is referred to this paper for a rigorous proof. $\mathbf{E}$ is the total energy content of the system, which may consist of more than one component and more than one phase. He also shows that

$$d\mathbf{F} = 0 \quad \text{at constant } p \text{ and } T \quad \text{(IV.25)}$$

is an equivalent criterion of equilibrium. Both these conditions for equilibrium follow at once from Eqs. (III.80) and (III.119) if we accept (without rigorous proof) the fact that these equations apply to any system at equilibrium however complex, just as well as to a simple system of one component and one phase. (Note, however, that we are still neglecting all forces except the pressure p.)

Since one is more immediately concerned with systems that are held at constant pressure and temperature than with isolated ones at constant S and V, the criterion expressed by Eq. (IV.25) is the better one to use. $\mathbf{F}$ is the *total* free energy of the system, and the derivative is with respect to all possible variations except those of p and T.

Let us now endeavor to get a little better picture of the meaning of this equation. A system may be in thermal equilibrium (no change in T) or mechanical equilibrium (no change in p), but it may still not have reached chemical or phase equilibrium. In other words, various changes are still possible, such as chemical reactions or transfer of material from one phase to another. All such changes will involve a decrease in the total free energy of the system; and when equilibrium is attained, $\mathbf{F}$ will be at its minimum value. This is expressed mathematically by Eq. (IV.25).

To give a more graphic picture of the meaning of Eq. (IV.25) let us consider a simple homogeneous chemical reaction such as

$$2A = A_2$$

where the composition of the system can be expressed by a single variable x, the mole fraction of the monomer. At a given pressure and tempera-

ture, the free energy would be expected to change continuously as shown in Fig. IV.1, the minimum point on the curve corresponding to the equilibrium composition. It is of interest to note that two different nonequilibrium states x_1 and x_3 have the same free energy; therefore, it is not in general correct to write as a criterion of equilibrium $\Delta F_{p,T} = 0$. Furthermore, although $F_1 > F_2$, the system would not spontaneously change from state 1 to state 2.
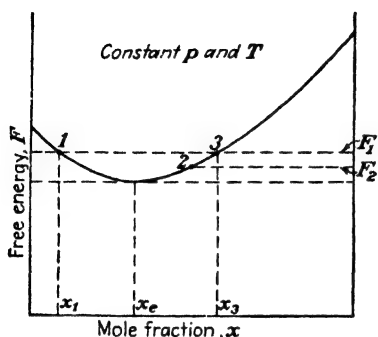
FIG. IV.1. Illustrating function, F, as a criterion of equilibrium.

Phase Equilibrium.—Equations similar to Eqs. (IV.21) and (IV.22) may be written for any number of phases of which the total system under consideration may be composed. Thus, using primes to indicate different phases, we may write

$$dF' = -S'\,dT + V'\,dp + \mu'_A\,dN'_A + \mu'_B\,dN'_B + \cdots + \mu'_N\,dN'_N \Big\}$$
$$dF'' = -S''\,dT + V''\,dp + \mu''_A\,dN''_A + \mu''_B\,dN''_B + \cdots + \mu''_N\,dN''_N \Big\} \quad (IV.26)$$

etc., for as many phases as there are in the system. It is obvious that pressure and temperature must be the same throughout if we are to have equilibrium (this assumes absence of any special membranes that might permit different pressures to exist), and so the primes may be omitted from these variables. If F represents the total free energy of the entire system, then

$$\mathbf{F} = \mathbf{F}' + \mathbf{F}'' + \mathbf{F}''' + \cdots + \mathbf{F}^z \qquad (IV.27)$$

Differentiating,

$$d\mathbf{F} = d\mathbf{F}' + d\mathbf{F}'' + d\mathbf{F}''' + \cdots + d\mathbf{F}^z \qquad (IV.28)$$

Combining Eqs. (IV.26) and (IV.28) and making use of the criterion of equilibrium expressed by Eq. (IV.25), we arrive at the relation

$$\mu'_A\,dN'_A + \mu'_B\,dN'_B + \cdots + \mu'_N\,dN'_N +$$
$$\mu''_A\,dN''_A + \mu''_B\,dN''_B + \cdots + \mu''_N\,dN''_N +$$
$$\cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot$$
$$\mu^z_A\,dN^z_A + \mu^z_B\,dN^z_B + \cdots + \mu^z_N\,dN^z_N = 0 \qquad (IV.29)$$

Since the total mass of each component remains constant (we are considering a closed system), we can write

$$dN'_A + dN''_A + dN'''_A + \cdots + dN^z_A = 0 \qquad (IV.30)$$

with a similar equation for each of the other components. To satisfy both Eqs. (IV.29) and (IV.30) it is necessary and sufficient 'that the following conditions be true:

$$\mu'_A = \mu''_A = \mu'''_A = \cdots = \mu^z_A$$
$$\mu'_B = \mu''_B = \mu'''_B = \cdots = \mu^z_B$$
$$\cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \quad \text{(IV.31)}$$
$$\mu'_N = \mu''_N = \mu'''_N = \cdots = \mu^z_N$$

In other words, the necessary condition for equilibrium is that the chemical potentials of a given component shall be equal in all the phases. This indicates that the chemical potential is a kind of driving force for mass transfer between phases or between portions of a given phase (homogeneous equilibrium) and equilibrium will be attained when, and only when, the potential differences are reduced to zero.

When equilibrium in a single phase (homogeneous equilibrium) is in question, application of the criterion expressed by Eq. (IV.25) to one of Eqs. (IV.26) gives

$$\mu_A \, dN_A + \mu_B \, dN_B + \cdots + \mu_N \, dN_N = 0 \quad \text{(IV.32)}$$

which is the fundamental equation for this case.

In arriving at the series of Eqs. (IV.31) we have specifically considered only the case where all components are present in all phases. There may be many cases in which this is not true and the equations will require slight modification, the nature of which is fairly obvious. Thus, if component A is present in phase ['] but not in phase [''], the equation $\mu'_A = \mu''_{A1}$ would drop out of the set of equations and similarly for any case of a component not being present in any phase.

Equations (IV.31) and (IV.32), first derived in this general form by Gibbs, form the fundamental basis for all deductions concerning equilibrium in chemical systems. Their further development to permit application to special cases consists in expressing the various μ's in terms of the variables of state, *i.e.*, in terms of pressure, temperature, and compositions.

Relation of Fugacity and Activity to the Chemical Potential.—Many authors prefer to treat chemical equilibria with the aid of these special functions, originally introduced by Lewis,[1] rather than using the chemical potentials directly, and hence it appears desirable to digress for a moment to establish the relationships between them.

In Chap. III the functions fugacity and activity were defined for a single component. The fugacity of any component of a solution f_i* may

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[1] LEWIS, G. N., *Proc. Am. Acad. Arts Sci.*, **37**, 49 (1901).

* Whenever it is necessary to distinguish between the fugacity or activity of a component of a solution and the same functions of the pure component, we shall place a bar over the symbol to indicate the case of solution.

be defined by the equation

$$d\mu_i = RT \, d \ln \bar{f}_i \qquad \text{(IV.33)}$$

Integrating between two isothermal states as in the case of a pure component,

$$\mu_i - \mu_i^\circ = RT \ln \frac{\bar{f}_i}{f_i^\circ} \qquad \text{(IV.34)}$$

where μ_i° and f_i° represent the chemical potential and fugacity, respectively, of component i in some arbitrarily chosen initial standard state of pressure and concentration. Hence, they are functions only of the temperature. For example, consider the system under study to be a mixture of gases at some high pressure p and temperature T, and let x_i be the mole fraction of any component of the solution. Now imagine the system to be expanded isothermally to some low pressure p° at which the gaseous solution may be regarded as an ideal gas. By analogy to the definition of the fugacity of a pure component, we may complete the definition of the fugacity of a component of a solution by making it equal to the partial pressure when the solution is expanded to the state of an ideal gas, or[1]

$$f_i^\circ = x_i p^\circ \qquad \text{(IV.35)}$$

Anticipating an equation to be derived later in the chapter,

$$\mu_i^\circ = RT \ln x_i + F_i^\circ \qquad \text{(IV.79)}$$

Introducing Eqs. (IV.35) and (IV.79) into Eq. (IV.34), we obtain the following relation between the fugacity and the chemical potential:

$$\mu_i = RT \ln \bar{f}_i + F_i^\circ - RT \ln p^\circ \qquad \text{(IV.36)}$$

where F_i° is the molal free energy of pure i at the pressure p°.

If the system in question is a solution of liquids, we can still imagine the solution to be isothermally vaporized and expanded to the state of an ideal gas, and the same equations apply. Even when solids are present, we can still use the same standard state because any solid can be assumed to have some vapor pressure and it is necessary only to take the pressure p° low enough to reduce the solid to an ideal gas. Usually, in the case of solutions containing liquids or solids, it will be more convenient to choose other standard states, a point that will be discussed later.

The activity of a component in a solution may be defined by the equation

$$\bar{a}_i = \frac{\bar{f}_i}{f_i^\circ} \qquad \text{(IV.37)}$$

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[1] The bar is omitted from f_i° because the fugacity of component i in a solution of ideal gases at pressure p° would be the same as the fugacity of pure i at the pressure $x_i p^\circ$. This follows from the concept of the ideal gas.

or more directly by the equation

$$\mu_i - \mu_i^\circ = RT \ln \bar{a}_i \tag{IV.38}$$

which is a combination of Eqs. (IV.34) and (IV.37). It is to be noted that the activity is always unity in the standard state. The main reason for the introduction of the activity function is that in certain cases we may determine a ratio of fugacities when it is not feasible to assign a numerical value to either one and it is convenient to give this ratio a name.

By substitution of Eqs. (IV.36) and (IV.38), respectively, in Eq. (IV.32) we obtain the following two equations for homogeneous equilibrium:

$$(RT \ln \bar{f}_A - RT \ln p^\circ + F_A^\circ)\, dN_A + (RT \ln \bar{f}_B - RT \ln p^\circ + F_B^\circ)\, dN_B$$
$$+ \cdots + (RT \ln \bar{f}_N - RT \ln p^\circ + F_N^\circ)\, dN_N = 0 \quad \text{(IV.39)}$$
$$(RT \ln \bar{a}_A + \mu_A^\circ)\, dN_A + (RT \ln \bar{a}_B + \mu_B^\circ)\, dN_B + \cdots$$
$$+ (RT \ln \bar{a}_N + \mu_N^\circ)\, dN_N = 0 \quad \text{(IV.40)}$$

If the standard state is any state of pure component, it is clear that

$$\mu_i = \frac{\partial \mathbf{F}}{\partial N_i} = F_i$$

where F_i is the molal free energy of pure i; and for this case we can substitute F_i° for μ_i° in Eqs. (IV.38) and (IV.40).

Substitution of Eq. (IV.36) in Eq. (IV.31) gives, for phase equilibrium,

$$\bar{f}_A' = \bar{f}_A'' = \cdots = \bar{f}_A^z \tag{IV.41}$$

with similar equations for the other components. Stated in words, a condition for equilibrium is that the fugacities of a given component shall be the same in all phases. Since activities are proportional to fugacities or to chemical potentials, it is evident that the activities of a given component are not necessarily equal in all the phases at equilibrium. If only one standard state is chosen for a given component, then the activities will be equal and we can write Eq. (IV.41) in terms of activity.

FREE ENERGY OF A HOMOGENEOUS SOLUTION OR PHASE

The next step in our development of general equations of equilibrium is to express the free energy of a homogeneous solution in terms of the variables of state. We shall now proceed to demonstrate one method by which this may be done.

For the molal free energy of any phase at constant temperature and composition,

$$dF = v \, dp \qquad \text{[from Eq. (IV.26)]}$$

or

$$F = \int_{p^\circ}^{p} v \, dp + F^\circ \qquad (\text{IV.42})$$

As before, p° is a pressure low enough so that the entire phase, whether initially gas, liquid, or solid, approaches the state of a mixture of ideal gases.

The definite integral in Eq. (IV.42) is the area under the v vs. p curve as the given phase is expanded at constant temperature from pressure p to p°. In the case of an initial gas solution, the integration might be performed algebraically if the relation between v and p could be expressed by an equation of state. In the case of an initial liquid or solid solution, the volume would not be a continuous function of p. Discontinuities would occur at the point where a gas phase first appears and at the point where the liquid or solid phase disappears; nevertheless, the integration could be performed graphically in this case.

We shall now proceed to evaluate F°, the free energy of a mixture of ideal gases. For the energy content of any homogeneous phase, we may write

$$E = E_A x_A + E_B x_B + \cdots + E_N x_N + \Delta E \qquad (\text{IV.43})$$

where E = molal energy of the total phase.
E_A, E_B, etc. = molal energies of components A, B, etc.
ΔE = energy change due to mixing at constant temperature and total pressure.

This is based on nothing but the first law and the fact that E is an extensive property. Now, when ideal gases are mixed at constant temperature, it is evident from the definition of an ideal gas that $\Delta E = 0$ (see also Chap. V). Also, for an ideal gas [Eq. (V.92), page 189],

$$v = v_A x_A + v_B x_B + \cdots + v_N x_N$$

where v = molal volume of the mixture.
v_A, v_B, etc. = molal volumes of pure components at the *pressure* and *temperature* of the mixture.
Multiplying this equation by the total pressure,

$$pv = p v_A x_A + p v_B x_B + \cdots + p v_N x_N \qquad (\text{IV.44})$$

Adding Eqs. (IV.43) and (IV.44) and putting $\Delta E = 0$,

$$E + pv = (E_A + p v_A) x_A + (E_B + p v_B) x_B + \cdots$$
$$+ (E_N + p v_N) x_N \quad (\text{IV.45})$$

or

$$H = H_A x_A + H_B x_B + \cdots + H_N x_N \qquad (\text{IV.46})$$

which may be abbreviated to

$$H = \Sigma H_i x_i \qquad (IV.47)$$

The H's of the individual components are all taken at the pressure and temperature of the mixture. By analogy to Eq. (IV.43),

$$S = S_A x_A + S_B x_B + \cdots + S_N x_N + \Delta S \qquad (IV.48)$$

From the nature of entropy it is clear that ΔS will not in general be zero when ideal gases are mixed at constant pressure and temperature.

As explained in Chap. I, the direct mixing of gases is an irreversible process. In order to find the entropy change during the mixing process it is necessary to devise a reversible process, and then the equation

$$\Delta S = \int_1^2 \frac{dQ}{T} \qquad (III.33)$$

is applicable, where 1 refers to the initial unmixed state and 2 the final mixed state. Such a process, involving the use of semipermeable membranes, has already been presented in Chap. I and will not be repeated here. For this special case the mixing box will have as many pistons and cylinders as there are gases to be mixed. The maximum work done by each gas as it expands isothermally from the initial pressure p to its partial pressure in the mixing chamber is as follows:

$$W_i = \int_v^{v^*} p \, dv_i$$

where v^* is the volume when the gas is at its partial pressure. Integrating,

$$W_i = N_i RT \ln \frac{v_i^*}{v_i}$$
$$= -N_i RT \ln \frac{\bar{p}_i}{p}$$
$$= -N_i RT \ln \frac{p x_i}{p}$$
$$= -N_i RT \ln x_i \qquad (IV.49)$$

The total work for all the gases is

$$\Sigma W = -RT(N_A \ln x_A + N_B \ln x_B + \cdots + N_N \ln x_N)$$

or, per mole of mixture,

$$\Sigma W = -RT \Sigma x_i \ln x_i \qquad (IV.50)$$

The mechanical work of pushing all the gases into the mixing chamber after they have been expanded to their partial pressures is exactly

balanced by the work of opposite sign done as the total pressure piston moves out, and hence these work terms cancel and may be omitted from the algebraic summation of all the work.

By the first law,

$$\Sigma W = \Sigma Q - \Delta E$$

and, since $\Delta E = 0$ for all isothermal changes of ideal gases,

$$\Sigma Q = -RT\Sigma x_i \ln x_i \tag{IV.51}$$

Utilizing Eq. (III.33),

$$\Delta S = -R\Sigma x_i \ln x_i \tag{IV.52}$$

This represents the increase of entropy when one mole of mixture is produced from the pure ideal gases at constant temperature and total pressure. Upon combining Eqs. (IV.52) and (IV.48), the entropy of an ideal-gas mixture is given by

$$S = S_A x_A + S_B x_B + \cdots + S_N x_N - R(x_A \ln x_A + \cdots + x_N \ln x_N)$$

or, in an abbreviated form,

$$S = \Sigma x_i S_i - R\Sigma x_i \ln x_i \tag{IV.53}$$

Now, since $F = H - TS$

then $F^\circ = H^\circ - TS^\circ$

$$F^\circ = \Sigma H_i^\circ x_i - T\Sigma x_i S_i^\circ + RT\Sigma x_i \ln x_i \tag{IV.54}$$

$$F^\circ = \Sigma x_i F_i^\circ + RT\Sigma x_i \ln x_i \tag{IV.55}$$

Finally, substituting Eq. (IV.55) in (IV.42), we arrive at the desired expression for the molal free energy of any homogeneous phase,

$$F = \int_{p^\circ}^{p} v\, dp + \Sigma x_i F_i^\circ + RT\Sigma x_i \ln x_i \tag{IV.56}$$

Noting that $\int_{p^\circ}^{p} v\, dp = \phi(p) - \phi(p^\circ)$ (at constant temperature)

and since we assume ideal gases at p°,

$$\phi(p^\circ) = RT \ln p^\circ$$

Hence, $$\int_{p^\circ}^{p} v\, dp = \int v\, dp - RT \ln p^\circ \tag{IV.57}$$

and (Eq. IV.56) may be put in the form

$$F = \int v\, dp + \Sigma x_i F_i^\circ + RT\Sigma x_i \ln x_i - RT \ln p^\circ \tag{IV.58}$$

It should be noted that the indefinite integral is evaluated along an isotherm.

ENERGY, ENTHALPY, AND ENTROPY OF A GAS MIXTURE

Before continuing with the development of equations for equilibrium, we shall digress for a moment to generalize some of the equations of Chap. III so that they are applicable to gas mixtures. Any one of these equations, as it stands, is applicable to a mixture as well as to a pure gas provided that we are considering the mixture at constant composition. Our present purpose is to introduce the composition as a variable.

Integrating the energy equation,

$$\left(\frac{\partial E}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v - p \qquad (\text{III}.78)$$

along an isotherm, between any volume v and a large volume v_∞ at which gases are ideal, gives

$$E - E^\circ = \int_{v_\infty}^{v} \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dv \qquad (\text{IV}.59)$$

Since E° is the energy of a mixture of ideal gases, we can write [see Eq. (IV.43)]

$$E^\circ = x_A E_A^\circ + x_B E_B^\circ + \cdots = \Sigma x_i E_i^\circ \qquad (\text{IV}.60)$$

and, for each individual gas, we have

$$E_i^\circ = \int_{T_0}^{T} C_v^\circ \, dT + E_{0i}^\circ \qquad (\text{IV}.61)$$

where T_0 is an arbitrary standard temperature and E_{0i}° is the energy of any individual gas at this temperature and at low pressure. E_A°, E_B°, . . . are the molal energies at the temperature and molal volume of the mixture.

The combination of Eqs. (IV.59), (IV.60), and (IV.61) gives a general expression for the energy of any gas mixture, which can be integrated with the aid of an equation of state (or pvT data) for the mixture and a knowledge of the ideal or low-pressure specific heat at constant volume for each gas.

In an exactly analogous manner we can obtain the corresponding equations for enthalpy and entropy by combination of the following equations:

$$H = H^\circ + \int_{p^\circ}^{p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp \qquad (\text{IV}.62)$$

$$H^\circ = \Sigma x_i H_i^\circ \qquad (\text{IV}.47)$$

$$H_i^\circ = \int_{T_0}^{T} C_p^\circ \, dT + H_{0i}^\circ \qquad (\text{IV}.63)$$

$$S = S^\circ - \int_{p^\circ}^{p} \left(\frac{\partial v}{\partial T}\right)_p dp \qquad (IV.64)$$

$$S^\circ = \Sigma x_i S_i^\circ - R\Sigma x_i \ln x_i \qquad (IV.53)$$

$$S_i^\circ = \int_{T_0}^{T} C_p^\circ d \ln T + S_{0i}^\circ \qquad (IV.65)$$

Combining Eqs. (IV.64), (IV.53), and (IV.65), we obtain the entropy equation

$$S = -\int_{p^\circ}^{p} \left(\frac{\partial v}{\partial T}\right)_p dp - R\Sigma x_i \ln x_i + \Sigma x_i \int_{T_0}^{T} C_p^\circ d \ln T + \Sigma x_i S_{0i}^\circ$$

S_{0i}° is the entropy of any component in the mixture when pure at p° and T_0.

By adding and subtracting $R \ln (p/p^\circ)$, from Eq. (IV.64) and combining with Eq. (IV.53), one obtains the following equation (for isothermal states):

$$S = \int_{p^\circ}^{p} \left[\frac{R}{p} - \left(\frac{\partial v}{\partial T}\right)_p\right] dp + \Sigma x_i S_i^\circ - R\Sigma x_i \ln x_i - R \ln \frac{p}{p^\circ} \qquad (IV.66)$$

This form has the advantage that the whole integral term vanishes for a system of ideal gases and therefore it is of the nature of a correction term and need not be evaluated very accurately. This is a device that can often be employed to advantage.

For a more rigorous and complete derivation of the equations for E H, S, and F of gas mixtures and a proof that the lower limit may be taken at the limit where p° approaches 0, reference may be made to papers by Beattie.[1]

EVALUATION OF CHEMICAL POTENTIALS AND FUGACITIES

Chemical Potential.—Since free energy is an extensive property, we may apply the general equations (IV.16) and (IV.17) to it and obtain

$$\mu_N = \frac{\partial F}{\partial N_N} = F - x_A \frac{\partial F}{\partial x_A} - x_B \frac{\partial F}{\partial x_B} - \cdots - x_{N-1} \frac{\partial F}{\partial x_{N-1}} \qquad (IV.67)$$

$$\mu_i = F + \frac{\partial F}{\partial x_i} - x_A \frac{\partial F}{\partial x_A} - x_B \frac{\partial F}{\partial x_B} - \cdots - x_{N-1} \frac{\partial F}{\partial x_{N-1}} \qquad (IV.68)$$

With the aid of Eq. (IV.56) we can now develop expressions for the differential coefficients in these two equations.

By differentiation of Eq. (IV.56) after writing it in expanded form,

$$\frac{\partial F}{\partial x_i} = \frac{\partial \left(\int_{p^\circ}^{p} v \, dp\right)}{\partial x_i} + RT \ln \frac{x_i}{x_N} + F_i^\circ - F_N^\circ \qquad (IV.69)$$

where $x_N = 1 - x_A - x_B \cdots - x_{N-1}$

[1] BEATTIE, J. A., *Phys. Rev.*, **31**, 680–690 (1928); **36**, 132–145 (1930).

Abbreviating $\left(1/RT\right)\int_{p^\circ}^{p} v\,dp$ by π_0, we have

$$\frac{\partial F}{\partial x_i} = RT\left(\frac{\partial \pi_0}{\partial x_i} + \ln\frac{x_i}{x_N}\right) + F_i^\circ - F_N^\circ \qquad \text{(IV.70)}$$

Equation (IV.70) can also be written

$$\frac{\partial F}{\partial x_i} = \int_{p^\circ}^{p} \frac{\partial v}{\partial x_i}\,dp + RT\ln\frac{x_i}{x_N} + F_i^\circ - F_N^\circ \qquad \text{(IV.71)}$$

For a binary solution Eq. (IV.70) becomes

$$\frac{\partial F}{\partial x} = RT\left(\frac{\partial \pi_0}{\partial x} + \ln\frac{x}{1-x}\right) + F_A^\circ - F_B^\circ \qquad \text{(IV.72)}$$

If we use Eq. (IV.58) instead of Eq. (IV.56), we get an equation of the same form as Eq. (IV.70) but with π in place of π_0, where $\pi = (1/RT)\int v\,dp$. With the aid of Eq. (IV.58) and the equation analogous to Eq. (IV.70) in π, Eqs. (IV.67) and (IV.68) may now be further developed, giving, respectively,

$$\mu_i = RT\left(\pi + \frac{\partial \pi}{\partial x_i} - x_A\frac{\partial \pi}{\partial x_A} - x_B\frac{\partial \pi}{\partial x_B} \cdots - x_{N-1}\frac{\partial \pi}{\partial x_{N-1}}\right)$$
$$+ RT\ln x_i + F_i^\circ - RT\ln p^\circ \quad \text{(IV.73)}$$

and

$$\mu_N = RT\left(\pi - x_A\frac{\partial \pi}{\partial x_A} - x_B\frac{\partial \pi}{\partial x_B} - \cdots - x_{N-1}\frac{\partial \pi}{\partial x_{N-1}}\right)$$
$$+ RT\ln x_N + F_N^\circ - RT\ln p^\circ \quad \text{(IV.74)}$$

Equations in terms of π_0 would be the same as these two equations with $RT\ln p^\circ$ omitted. For the special case of binary solutions, Eqs. (IV.73) and (IV.74) reduce, respectively, to

$$\mu_A = RT\left[\pi + (1-x)\frac{\partial \pi}{\partial x}\right] + RT\ln x + F_A^\circ - RT\ln p^\circ \quad \text{(IV.75)}$$

$$\mu_B = RT\left(\pi - x\frac{\partial \pi}{\partial x}\right) + RT\ln(1-x) + F_B^\circ - RT\ln p^\circ \quad \text{(IV.76)}$$

Equivalent equations for μ_i and μ_N in a somewhat simpler form can be obtained from an equation analogous to Eq. (IV.56) for the total free energy of ΣN moles of any phase. Multiplying this equation by ΣN and noting that $x_i = N_i/\Sigma N$, one gets

$$\mathbf{F} = \int_{p^\circ}^{p} V\,dp + \Sigma N_i F_i^\circ + RT\Sigma N_i \ln\frac{N_i}{\Sigma N} \qquad \text{(IV.77)}$$

Then, since
$$\mu_i = \frac{\partial \mathbf{F}}{\partial N_i}$$

we have, by differentiation of Eq. (IV.77),

$$\mu_i = \int_{p^\circ}^{p} \frac{\partial V}{\partial N_i}\, dp + RT \ln x_i + F_i^\circ \qquad \text{(IV.78)}$$

and the equation for μ_N is of exactly the same form. As p decreases and approaches the limiting value p° where all gases are assumed ideal, Eq. (IV.78) reduces to

$$\mu_i = RT \ln x_i + F_i^\circ \qquad \text{(IV.79)}$$

which is the special form of Eq. (IV.78) applying to an ideal-gas solution.

The equivalence of Eq. (IV.78) and the equation in terms of π_0 that is analogous to (IV.73) is readily shown as follows: From Eq. (IV.17) it is evident that

$$\bar{v}_i = \frac{\partial V}{\partial N_i} = v + \frac{\partial v}{\partial x_i} - x_A \frac{\partial v}{\partial x_A} - x_B \frac{\partial v}{\partial x_B} \cdots - x_{N-1} \frac{\partial v}{\partial x_{N-1}} \qquad \text{(IV.80)}$$

Equation (IV.78) can then be written

$$\mu_i = \int_{p^\circ}^{p} \left(v + \frac{\partial v}{\partial x_i} - x_A \frac{\partial v}{\partial x_A} - x_B \frac{\partial v}{\partial x_B} - \cdots - x_{N-1} \frac{\partial v}{\partial x_{N-1}} \right) dp \\ + RT \ln x_i + F_i^\circ \qquad \text{(IV.81)}$$

Since

$$RT\, \pi_0 = \int_{p^\circ}^{p} v\, dp \qquad \text{(IV.82)}$$

and

$$RT\, \frac{\partial \pi_0}{\partial x_i} = \int_{p^\circ}^{p} \frac{\partial v}{\partial x_i}\, dp \qquad \text{(IV.83)}$$

(IV.81) is readily transformed to Eq. (IV.73) in terms of π_0.

Fugacity and Activity.—From Eqs. (IV.36) and (IV.73),

$$\ln f_i = \ln x_i + \pi + \frac{\partial \pi}{\partial x_i} - x_A \frac{\partial \pi}{\partial x_A} - x_B \frac{\partial \pi}{\partial x_B} \cdots - x_{N-1} \frac{\partial \pi}{\partial x_{N-1}} \qquad \text{(IV.84)}$$

From Eqs. (IV.36) and (IV.74) the corresponding equation for $\ln f_N$ is obtained.

From Eqs. (IV.36) and (IV.78),

$$\ln f_i = \frac{1}{RT} \int_{p^\circ}^{p} \frac{\partial V}{\partial N_i}\, dp + \ln x_i + \ln p^\circ \qquad \text{(IV.85)}$$

Equations (IV.84) and (IV.85) are merely two forms of the same equation. Other forms that may prove useful in certain cases can also be obtained. For example, we can remove the lower limit from the integral of Eq. (IV.85) somewhat as was done in the case of Eq. (IV.56).

Since the gas is ideal at the pressure p°,

$$\frac{\partial V}{\partial N_i} = v_i = \frac{RT}{p^\circ}$$

and the function of the lower limit reduces to $- \ln p°$, and Eq. (IV.85) becomes

$$\ln f_i = \frac{1}{RT} \int \frac{\partial V}{\partial N_i} dp + \ln x_i \qquad (IV.86)$$

For pure component i at p and T,

$$\ln \frac{f_i}{f_i°} = \frac{1}{RT} \int_{p°}^{p} v_i \, dp \qquad (III.140)$$

Combining Eq. (III.140) with Eq. (IV.85) and noting that $f_i° = p°$,

$$\ln f_i = \frac{1}{RT} \int_{p°}^{p} (\bar{v}_i - v_i) \, dp + \ln f_i + \ln x_i \qquad (IV.87)$$

Eq. (IV.85) is also readily transformed to

$$\ln f_i = \frac{1}{RT} \int_{p°}^{p} \left(\bar{v}_i - \frac{RT}{p} \right) dp + \ln p x_i \qquad (IV.88)$$

Equation (IV.88) for the fugacity of a component of a solution is the analogue of Eq. (III.142) for the fugacity of a pure substance; in fact, it reduces to Eq. (III.142) at the limit where $x = 1$. Either Eq. (IV.87) or (IV.88) offers a very satisfactory way to define the fugacity of a component of a solution because the quantities $\bar{v}_i - v_i$ and $\bar{v}_i - (RT/p)$ have been shown[1] to approach finite values as p approaches zero, like the function α used in evaluating fugacity of a single component. They do not approach the value zero at the limit as some have erroneously assumed. This can be demonstrated either by an extrapolation of existing data on the compressibility of gas mixtures or by an equation of state for mixtures.

From Eq. (IV.84) or (IV.85) or the other forms of these equations it is readily seen that, for the special case of $x_i = 1$,

$$\ln f_i = \pi_i$$

or
$$f_i = e^{\pi_i} \qquad (IV.89)$$

Equations for activity corresponding to the various fugacity equations can be obtained either from the latter and Eq. (IV.37) or directly from Eq. (IV.38). For example, the equation corresponding to Eq. (IV.85) is

$$\ln \bar{a}_i = \frac{1}{RT} \int_{p°}^{p} \bar{v}_i \, dp \qquad (IV.90)$$

Note on Standard States.—It seems obvious that one would avoid confusion if he always adhered to one state as the standard state of a given substance and never used any other. A simple standard state

[1] GILLESPIE, L. J., *Phys. Rev.*, **34**, 352 (1929).

would be that of the substance when pure at the given temperature and at a pressure of 1 atm.   Unfortunately, owing to the fact that only very limited data are available for some systems so that one cannot go to the limit of pure components, it becomes necessary to choose other standard states, and this has been a source of a great deal of confusion to students of thermodynamics.   For example, if one is concerned with relatively dilute alcohol-water solutions at elevated temperatures, the data are lacking that would enable one to proceed from the given concentration to pure alcohol at the same temperature.   In such a case it is customary to base the activity on an extrapolation to the other limit, *viz.*, an infinitely dilute solution.   Thus one may complete the definition of activity, given partially by Eq. (IV.38), by writing

$$\lim_{x \to 0} \frac{\bar{a}}{x} = 1 \qquad (IV.91)$$

In place of x, mole fraction, one could also use the molality m or the molal concentration.

It is evident from Eq. (IV.37) that the activity is unity in the standard state and therefore that the standard state involved in the definition based on Eq. (IV.91) is obviously not one of infinite dilution.   To make this point clearer, let us take a simple specific case, *viz.*, that of a volatile solute which obeys Henry's law in dilute solution, and let us also assume that the vapor is an ideal gas.   Then, since fugacity equals pressure for an ideal gas,

$$\bar{a} = \frac{\bar{p}}{p^\circ} \qquad (IV.92)$$

For the infinitely dilute solution,

$$\bar{a}^\infty = \frac{\bar{p}^\infty}{p^\circ} \qquad (IV.93)$$

but, by Eq. (IV.91), $\bar{a}^\infty = x^\infty$

$$\therefore \bar{a} = \frac{\bar{p}x^\infty}{\bar{p}^\infty} \qquad (IV.94)$$

But, by Henry's law, $\dfrac{x^\infty}{\bar{p}^\infty} = k$

and hence $\bar{a} = k\bar{p} \qquad (IV.95)$

Since $\bar{a} = 1$ in the standard state, this state is one for which the partial pressure $= 1/k$.

A solution of ethanol in water containing 0.0177 mole fraction EtOH has a partial vapor pressure of EtOH of 3.65 mm. at 25°C., and Henry's law is closely followed.

$$\therefore k = \frac{0.0177}{3.65} \qquad \text{or} \qquad \frac{1}{k} = 206 \text{ mm.}$$

The vapor pressure of pure EtOH at 25°C. = 59 mm., and hence one sees that the state for a vapor pressure of 206 mm. is a purely fictitious one.[1]

Since $x/\bar{p} = k$ for any solution up to the limit at which Henry's law is obeyed, it follows that $\bar{a} = x$ up to this same limit (or $\bar{a} = m$, if concentration were expressed in terms of molality). The fact that this simple relationship results is one of the chief reasons for defining the standard state on the basis of Eq. (IV.91). One could avoid fictitious standard states by letting $\bar{a}/x$ approach 100 instead of 1.0 as in Eq. (IV.91) or better still by choosing the standard state as some low concentration, for example, $x = 0.01$ or $x = 0.001$ where Henry's law could be assumed with sufficient accuracy for practical purposes.

Adams[2] proposes to combine Eqs. (IV.38) and (IV.91), giving the following single equation completely defining activity for a nondissociating solute:

$$\bar{a}_1 = \lim_{x \to 0} \frac{x}{c^{(\mu - \mu_1)/RT}} \qquad (IV.96)$$

$\bar{a}_1$ is the activity of any solute at a given concentration x_1 where the chemical potential is μ_1. By taking a series of concentrations x, where the corresponding potential is μ, and determining $\mu - \mu_1$ and finding the limit either by analytical or graphical means, the value of $\bar{a}_1$ is obtained. For further details and for extensions to systems containing dissociating solutes, refer to Adams's paper.

Temperature, Pressure, and Composition Coefficients.—The chemical potentials, fugacities, and activities are functions of pressure, temperature, and composition. In this section we shall develop the differential coefficients expressing the rates of change with respect to these variables.

The change of chemical potential with composition is readily obtained by differentiation of Eq. (IV.78), giving

$$\left(\frac{\partial \mu_i}{\partial x_i} \right)_{p,T} = \int_{p^\circ}^{p} \frac{\partial \bar{v}_i}{\partial x_i} \, dp + \frac{RT}{x_i} \qquad (IV.97)$$

An alternative form is obtained by differentiating Eq. (IV.81), giving

$$\frac{\partial \mu_i}{\partial x_i} = (1 - x_i) \int_{p^\circ}^{p} \frac{\partial^2 v}{\partial x_i^2} \, dp + \frac{RT}{x_i} \qquad (IV.98)$$

Now,
$$\left(\frac{\partial \mu_i}{\partial p} \right)_{T,x} = \left[\frac{\partial \left(\frac{\partial F}{\partial \bar{N}_i} \right)_{p,T}}{\partial p} \right]_{T,x}$$

[1] If the solution were an ideal one, the standard state would be that of the pure component.

[2] ADAMS, L. H., *Chem. Rev.*, **19**, 1–26 (1936).

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,x} = \frac{\partial \left(\frac{\partial \mathbf{F}}{\partial p}\right)_{T,x}}{\partial N_i}$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,x} = \frac{\partial V}{\partial N_i} = \bar{v}_i \qquad (\text{IV.99})$$

This also follows directly from Eq. (IV.78) by differentiation with respect to p.

Similarly, since $\partial \mathbf{F}/\partial T = -\mathbf{S}$,

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,x} = \frac{\partial^2 \mathbf{F}}{\partial N_i \, \partial T} = -\frac{\partial \mathbf{S}}{\partial N_i} = -\bar{S}_i \qquad (\text{IV.100})$$

Now since
$$\mathbf{F} = \mathbf{H} - T\mathbf{S}$$

by differentiation,
$$\frac{\partial \mathbf{F}}{\partial N_i} = \mu_i = \bar{H}_i - T\bar{S}_i$$

Combining with Eq. (IV.100),

$$\frac{\partial \mu_i}{\partial T} = \frac{1}{T}(\mu_i - \bar{H}_i) \qquad (\text{IV.101})$$

From the relation between fugacity and chemical potential as expressed by Eq. (IV.36) it is readily seen that

$$\left(\frac{\partial \mu}{\partial x}\right)_{p,T} = RT \frac{\partial \ln \bar{f}}{\partial x} \qquad (\text{IV.102})$$

and
$$\left(\frac{\partial \mu}{\partial p}\right)_{T,x} = RT \frac{\partial \ln \bar{f}}{\partial p} \qquad (\text{IV.103})$$

and
$$\left(\frac{\partial \mu}{\partial T}\right)_{p,x} = RT \frac{\partial \ln \bar{f}}{\partial T} + R \ln \bar{f} + \frac{\partial F^\circ}{\partial T} - R \ln p^\circ \qquad (\text{IV.104})$$

From Eqs. (IV.102) and (IV.97),

$$\frac{\partial \ln \bar{f}_i}{\partial x_i} = \frac{1}{RT}\int_{p^\circ}^{p} \frac{\partial \bar{v}_i}{\partial x_i} dp + \frac{1}{x_i} \qquad (\text{IV.105})$$

From Eqs. (IV.103) and (IV.99), $\dfrac{\partial \ln \bar{f}_i}{\partial p} = \dfrac{\bar{v}_i}{RT}$ (IV.106)

From (IV.104) and (IV.100) and the fact that $\dfrac{\partial F^\circ}{\partial T} = -S^\circ$,

$$RT \frac{\partial \ln \bar{f}_i}{\partial T} = -\bar{S}_i - R \ln \bar{f}_i + S_i^\circ + R \ln p^\circ \qquad (\text{IV.107})$$

But since
$$\mathbf{F} = \mathbf{H} - T\mathbf{S}$$

and hence
$$\bar{F} = \mu = \bar{H} - T\bar{S} \qquad (\text{IV.108})$$

Eq. (IV.107) becomes

$$RT\frac{\partial \ln f_i}{\partial T} = \frac{\bar{F}_i}{T} - \frac{\bar{H}_i}{T} - R \ln f_i - \frac{F_i^\circ}{T} + \frac{H_i^\circ}{T} + R \ln p^\circ$$

But, by Eq. (IV.36),

$$\frac{\bar{F}_i}{T} - R \ln f_i - \frac{F_i^\circ}{T} + R \ln p^\circ = 0$$

$$\therefore \quad \frac{\partial \ln f_i}{\partial T} = -\frac{\bar{H}_i - H_i^\circ}{RT^2} \tag{IV.109}$$

Differentiating Eq. (IV.38) and combining with Eq. (IV.100), one gets the analogous equation for change of activity with temperature, *viz.*,

$$\frac{\partial \ln \bar{a}_i}{\partial T} = -\frac{\bar{H}_i - \bar{H}_i^\circ}{RT^2} \tag{IV.110}$$

The equations for rate of change of activity with p and x are the same as the corresponding equations for fugacity since the fugacity in the standard state is a function of temperature only. The temperature coefficient, however, is slightly different, as just shown.

Equation (IV.110) is clear as long as the standard state is that of pure component and $\bar{H}_i^\circ = H_i^\circ$; but when the standard state is defined by Eq. (IV.91), then the differentiation is ambiguous and the meaning of $\bar{H}_i^\circ$ is not clear without further discussion. Thus not only is the standard state a fictitious one, but the fictitious concentration is different for each temperature and the meaning of $\partial \mu / \partial T$ at constant concentration is certainly not clear. If the standard state is defined by arbitrarily choosing a certain concentration (see page 123) for all temperatures, then $\bar{H}_i^\circ$ is the partial molal enthalpy at that concentration. If, on the other hand, $\bar{a}$ is defined by Eq. (IV.96), then one still obtains Eq. (IV.110) and $\bar{H}_i^\circ$ refers to the limiting value approached by $\bar{H}_i$ as x approaches zero.

It is of interest to note that Eq. (IV.110) may also be obtained directly from Eq. (IV.96) by differentiation.

IDEAL SOLUTIONS

Applying Eq. (IV.8) for any extensive property, to the case of volume,

$$v = \bar{v}_A x_A + \bar{v}_B x_B + \cdots + \bar{v}_N x_N \tag{IV.111}$$

In general, the partial molal volumes are functions of the composition of the solution; but in some cases the change with composition is slight, and we may, for simplicity, define a special type of solution in which these quantities are constants independent of composition. Such a solution is known as an "ideal solution." The concept of the ideal solution, like that of the ideal gas, is a limiting case that all actual solutions can only approach more or less closely, depending on conditions.

If the various components of an ideal solution are stable in the pure state at the pressure and temperature of the solution, then

$$\bar{v}_i = \frac{\partial V}{\partial N_i} = \frac{V}{N_i} = v_i,$$

the molal volume of pure i at p and T. For this case, Eq. (IV.111) becomes

$$v = v_A x_A + v_B x_B + \cdots + v_N x_N \qquad \text{(IV.112)}$$

or the volumes of the components are additive. Thus Eq. (IV.112) might be applied to a mixture of gases such as nitrogen and hydrogen, at room temperature and at any pressure, but it could not be strictly applied to a mixture of hydrogen and ammonia at any pressure greater than the vapor pressure of ammonia at the temperature in question. Generalizing, one could state that Eq. (IV.112) might be applied to any gaseous mixture at any pressure provided that the temperature concerned is greater than the critical temperature of all components. If the temperature is below the critical temperature of any component, then Eq. (IV.112) applies only up to the vapor pressure of that component. It applies to liquid mixtures only when the temperature is below the boiling point (for the pressure in question) of the most volatile component, for at any higher temperature this component cannot exist in the free state as a liquid at the pressure of the mixture. Obviously, it can never be strictly applied to the case of liquid-vapor phase equilibrium because one or the other of those conditions will be violated for some component. Thus, for a binary liquid-vapor equilibrium, each component is of necessity stable in only one of the phases when pure at the pressure and temperature of the solution. In the special case of liquid-vapor equilibria at a temperature below the critical temperature of all components, it will be convenient to define an ideal liquid solution as one for which Eq. (IV.112) applies where v_A, v_B, etc., are taken to mean the volumes of the pure components at the temperature of the solution, but each at its *respective vapor pressure*. This is allowable because the effect of pressure on liquid volumes is so small. Obviously, a similar definition for a vapor solution would be absurd.

For the special case of ideal solutions and when the component in question is stable in the given phase at the pressure and temperature of the solution, Eq. (IV.78) becomes

$$\mu_i = \int_{p^o}^{p} v_i \, dp + RT \ln x_i + F_i^o$$

but since

$$\int_{p^o}^{p} v_i \, dp = F_i - F_i^o$$

Eq. (IV.78) reduces to

$$\mu_i = F_i + RT \ln x_i \qquad \text{(IV.113)}$$

and Eq. (IV.87) reduces to

$$\ln \bar{f}_i = \ln f_i + \ln x_i \tag{IV.114}$$

or

$$\bar{f}_i = x_i f_i \tag{IV.115}$$

This simple relationship has been widely used, but one should always bear in mind that it applies only when the volumes are additive and when the component in question is stable in the pure state at the pressure and temperature of the mixture. It is analogous to the relationship usually called "Raoult's law," *viz.*, $\bar{p}_i = x_i p_i$, which applies to an ideal liquid solution when the vapor is an ideal gas.

From Eqs. (IV.115), (IV.109), and (III.146), one finds that

$$\bar{H}_i = H_i$$

and hence

$$H = H_A x_A + H_B x_B + \cdots \tag{IV.116}$$

In other words, an ideal solution is also one for which there is no heat of mixing since the enthalpies are additive.

From Eqs. (IV.38) and (IV.113) it is readily seen that

$$\bar{a}_i = k x_i \tag{IV.117}$$

for an ideal solution; and if the standard state upon which the activity is based is that of the pure component at the same temperature and total pressure, $k = 1$. This is generally used only for liquid solutions where the change of activity with pressure is small and can usually be neglected. The variation of $\bar{a}/x$ from unity as x decreases from 1.0 is a convenient measure of the departure of a solution from ideality. Some authors use Eq. (IV.117) as the definition of an ideal solution.

From Eq. (IV.111), for the case where x_N is eliminated in terms of the other mole fractions, we have

$$\frac{\partial v}{\partial x_i} = \bar{v}_i - \bar{v}_N \tag{IV.118}$$

and, from Eq. (IV.112),

$$\frac{\partial v}{\partial x_i} = v_i - v_N \tag{IV.119}$$

From Eqs. (IV.83) and (IV.119),

$$\frac{\partial \pi_0}{\partial x_i} = \frac{1}{RT} \int_{p^\circ}^{p} (v_i - v_N) \, dp \tag{IV.120}$$

with a similar equation for $\partial \pi / \partial x$. By differentiation of Eq. (IV.120) and the corresponding equation in π, we have

$$\frac{\partial^2 \pi_0}{\partial x_i^2} = \frac{\partial^2 \pi}{\partial x_i^2} = 0 \tag{IV.121}$$

SPECIAL CASES OF PHASE EQUILIBRIUM

The Phase Rule.—Equations (IV.31) define the general conditions for equilibrium in a system composed of N components and Z phases, each component being present in each phase. For each phase, at first thought there would appear to be, according to Eq. (IV.26), $(N + 2)$ independent variables; but if the molal masses of the components were all increased in the same ratio, there would be no change in composition and no change in state but only a change in amount. Clearly, the mass ratios, or compositions, must be changed to change the state of the phase, and there will be $N - 1$ independent mass ratios, or composition variables. Therefore, the total number of variables defining the state of the whole system of N components in Z phases = $Z(N - 1) + 2$. The equilibrium equations (IV.31) impose $Z - 1$ conditions that must be met by each component or a total of $N(Z - 1)$ conditions. The total number of variables − the total number of conditions imposed by the equations equals D, the degrees of freedom of the system, or

$$Z(N - 1) + 2 - N(Z - 1) = D$$

or
$$D = N - Z + 2 \qquad (IV.122)$$

This is the famous phase rule first enunciated by Gibbs in 1875. The derivation we have given is, in principle, the same as that of Gibbs, but rigorousness has been sacrificed to simplicity.

If any component is missing from any phase, there will be one less composition variable for that phase and also one less condition equation, so that the rule still holds for all special cases of this type.

Differential Equations for Two-component Two-phase Systems.— The rest of our discussion of phase equilibrium will be limited to systems whose maximum complexity is two components and two phases. We shall therefore proceed to develop the differential equations pertaining to this case so that they may serve as the starting point for still further reduction to special cases. For this case the general equilibrium conditions expressed by Eq. (IV.31) become

$$\mu_A' = \mu_A'' \qquad (IV.123)$$
$$\mu_B' = \mu_B'' \qquad (IV.124)$$

Let A be the component whose mole fraction is x. From the calculus and the fact that μ is a function of p, T, and x,

$$\frac{\partial \mu_A'}{\partial x'} dx' + \frac{\partial \mu_A'}{\partial p} dp + \frac{\partial \mu_A'}{\partial T} dT = \frac{\partial \mu_A''}{\partial x''} dx'' + \frac{\partial \mu_A''}{\partial p} dp + \frac{\partial \mu_A''}{\partial T} dT \quad (IV.125)$$

Substituting the values of the coefficients as given by Eqs. (IV.97), (IV.99), and (IV.100), one obtains the general differential equation

relating pressure, temperature, and the composition of both phases for a two-component two-phase system, *viz.*,

$$\left(\int_{p^o}^{p} \frac{\partial \bar{v}_A'}{\partial x'} \, dp + \frac{RT}{x'} \right) dx' + \bar{v}_A' \, dp - \bar{S}_A' \, dT$$

$$= \left(\int_{p^o}^{p} \frac{\partial \bar{v}_A''}{\partial x''} \, dp + \frac{RT}{x''} \right) dx'' + \bar{v}_A'' \, dp - \bar{S}_A'' \, dT \quad \text{(IV.126)}$$

This has been given in various other forms. For example, another form is obtained by using Eqs. (IV.98) and (IV.17). Also, by making use of Eq. (IV.101), the dT terms can be combined to give

$$\frac{\bar{H}_A'' - \bar{H}_A'}{T} \, dT$$

A useful form of the equation, involving the differential of the composition of one of the phases only, is obtained as follows:

From Eqs. (IV.67) and (IV.68),

$$\mu_B = F - x \frac{\partial F}{\partial x} \quad \text{(IV.127)}$$

and
$$\mu_A = F + (1 - x) \frac{\partial F}{\partial x} \quad \text{(IV.128)}$$

Then since
$$\mu_B' = \mu_B'' \quad \text{(IV.129)}$$
and
$$\mu_A' = \mu_A'' \quad \text{(IV.130)}$$

we have
$$F' - x' \frac{\partial F'}{\partial x'} = F'' - x'' \frac{\partial F''}{\partial x''} \quad \text{(IV.131)}$$

and
$$F' + (1 - x') \frac{\partial F'}{\partial x'} = F'' + (1 - x'') \frac{\partial F''}{\partial x''} \quad \text{(IV.132)}$$

Comparing Eqs. (IV.131) and (IV.132),

$$\frac{\partial F'}{\partial x'} = \frac{\partial F''}{\partial x''} \quad \text{(IV.133)}$$

Differentiating (IV.131),

$$dF' - x'd \frac{\partial F'}{\partial x'} - \frac{\partial F'}{\partial x'} \, dx' = dF'' - x''d \frac{\partial F''}{\partial x''} - \frac{\partial F''}{\partial x''} \, dx'' \quad \text{(IV.134)}$$

Utilizing Eq. (IV.133) and the fact that

$$dF = \dot{v} \, dp - S \, dT + \frac{\partial F}{\partial x} \, dx \quad \text{(IV.135)}$$

Eq. (IV.134) can be put in the form

$$(v'' - v') \, dp - (S'' - S') \, dT - (x'' - x') \, d \frac{\partial F'}{\partial x'} = 0 \quad \text{(IV.136)}$$

From the calculus,

$$d \frac{\partial F'}{\partial x'} = \frac{\partial^2 F'}{\partial x' \, \partial p} \, dp + \frac{\partial^2 F'}{\partial x' \, \partial T} \, dT + \frac{\partial^2 F'}{\partial x'^2} \, dx' \quad \text{(IV.137)}$$

Substituting Eq. (IV.137) in Eq. (IV.136), we obtain the relation sought, viz.,

$$\left[v'' - v' - (x'' - x') \frac{\partial v'}{\partial x'} \right] dp - \left[S'' - S' - (x'' - x') \frac{\partial S'}{\partial x'} \right] dT$$
$$- (x'' - x') \frac{\partial^2 F'}{\partial x'^2} dx' = 0 \quad (IV.138)$$

By elimination of $\partial F'/\partial x'$ instead of $\partial F''/\partial x''$ from Eq. (IV.134) one obtains the analogous equation for the other phase,

$$\left[v'' - v' - (x'' - x') \frac{\partial v''}{\partial x''} \right] dp - \left[S'' - S' - (x'' - x') \frac{\partial S''}{\partial x''} \right] dT$$
$$- (x'' - x') \frac{\partial^2 F''}{\partial x''^2} dx'' = 0 \quad (IV.139)$$

The expression $v'' - v' - (x'' - x')(\partial v'/\partial x')$ has a simple physical meaning; it is the net change in volume that results when one mole of the second phase ['] is condensed into such a large amount of the first phase ['] that the composition of the latter phase is not appreciably changed. This may be proved as follows:

When one mole of the second phase is added to N moles of the first, the molal volume of the latter will tend to change owing to a change in composition, and after the process, the volume of the first phase can be represented by the expression

$$v' + \frac{\partial v'}{\partial x'} \Delta x' + \cdots$$

Higher terms can be neglected if we consider N to be very large compared with 1.

$$\Delta x' = \text{final composition of first phase} - \text{initial composition}$$
$$= \frac{Nx' + x''}{N + 1} - x'$$
$$= \frac{x'' - x'}{N + 1}$$

Therefore

$$\text{Final molal volume of first phase} = v' + \frac{x'' - x'}{N + 1} \frac{\partial v'}{\partial x'}$$

or $$\text{Total volume} = (N + 1)v' + (x'' - x') \frac{\partial v'}{\partial x'}$$

Since the second phase is completely condensed, this is also the final total volume.

$$\text{Original total volume} = v'' + Nv'$$

Then Δv, the net volume change for the process, is given by

$$\Delta v = (N + 1)v' + (x'' - x')\frac{\partial v'}{\partial x'} - v'' - Nv'$$

$$= -\left[v'' - v' - (x'' - x')\frac{\partial v'}{\partial x'}\right]$$

Similarly, the expression $[S'' - S' - (x'' - x')(\partial S'/\partial x')]$ is equal to $-\Delta S$, the change in entropy when one mole of the second phase is condensed into a large (infinite at the limit) amount of the first phase. Conversely, ΔS is the entropy change when a mole of phase $['']$ is vaporized from a very large amount of the first phase, and $T\,\Delta S$ is generally called the "differential latent heat of vaporization" when the two phases in question are liquid and vapor.

From the equation analogous to Eq. (IV.72) in terms of π and Eq. (IV.133) we have

$$RT\left(\frac{\partial \pi'}{\partial x'} + \ln \frac{x'}{1-x'}\right) = RT\left(\frac{\partial \pi''}{\partial x''} + \ln \frac{x''}{1-x''}\right)$$

or

$$\frac{x''}{1-x''} = \frac{x'}{1-x'}\,e^{\left[\frac{\partial \pi'}{\partial x'} - \frac{\partial \pi''}{\partial x''}\right]} \tag{IV.140}$$

This is a general equation directly relating the compositions of the coexisting phases at equilibrium.

From Eqs. (IV.76) and (IV.129),

$$\pi' + \ln(1 - x') - x'\frac{\partial \pi'}{\partial x'} = \pi'' + \ln(1 - x'') - x''\frac{\partial \pi''}{\partial x''} \tag{IV.141}$$

Comparing Eqs. (IV.140) and (IV.141),

$$\frac{x''}{x'} = e^{\left[\pi' + (1-x')\frac{\partial \pi'}{\partial x'}\right] - \left[\pi'' + (1-x'')\frac{\partial \pi''}{\partial x''}\right]} \tag{IV.142}$$

It is readily shown that $\pi = (N_A + N_B)\pi$, or that π is an extensive property and therefore

$$\bar{\pi}_A = \frac{\partial \pi}{\partial N_A}$$

$$= \pi + (1 - x)\frac{\partial \pi}{\partial x}$$

Thus we may put Eq. (IV.142) in the form

$$\frac{x''}{x'} = e^{\bar{\pi}_A' - \bar{\pi}_A''} \tag{IV.143}$$

Note that

$$\bar{\pi}_A = \frac{1}{RT}\int \bar{v}_A\,dp$$

Thermodynamic Method of Determining Phase Equilibrium.—The usual method of investigating experimentally a phase equilibrium is to bring the two phases in contact and make certain observations while

t and x constant

μ of solid phase

μ of solution phase

Freezing point

Pressure
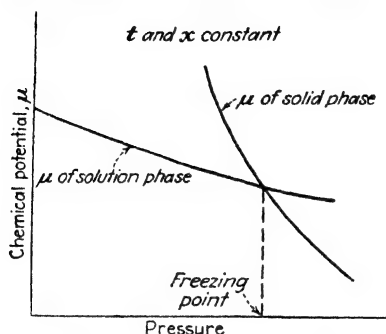
Fig. IV.2.—Indirect, or thermodynamic, method of determining phase equilibrium.

they coexist. There are many variations in detail between different methods, but all depend on establishing an equilibrium between the phases. Adams[1] has developed an indirect method that is an application of some of the equations presented in the previous section. It is indirect because equilibrium between the phases does not have to be established. This has certain advantages, particularly in the case of equilibria at high pressures.

Consider the case of equilibrium between a solid phase and a liquid solution and the effect of pressure on it at a given temperature and composition of the solution. From Eqs. (IV.123) and (IV.99) we have

$$\mu'_A = \mu''_A$$

and

$$\left(\frac{\partial \mu_A}{\partial p}\right)_{T,x} = \bar{v}_A$$

Then

$$\mu_A = \mu^o_A + \int_{p^o}^{p} \bar{v}_A \, dp$$

By volume measurements on each phase alone at a series of pressures and compositions, one can establish a curve of μ vs. p for that phase. The two curves are then plotted, and their intersection determines an equilibrium point in accordance with Eq. (IV.123) (see Fig. IV.2). It is to be noted that the identity of the solid phase must have been established by some other means. Thus, in the case investigated by Adams, the system was $NaCl-H_2O$, and the stable solid phase under his conditions was ice VI.

Duhem Equation.—For a binary system, Eq. (IV.9) in terms of free energy as the property becomes

$$x \, d\mu_A = -(1 - x) \, d\mu_B \qquad (IV.144)$$

Now, since μ_A and μ_B can be expressed as functions of T and x (p is a dependent variable), at constant temperature we have

$$x \left(\frac{\partial \mu_A}{\partial x}\right)_T = -(1 - x) \left(\frac{\partial \mu_B}{\partial x}\right)_T \qquad (IV.145)$$

[1] Adams, L. H., *J. Am. Chem. Soc.*, **53**, 3769–3813 (1931).

or
$$x\left(\frac{\partial\mu_A}{\partial x}\right)_T = (1 - x)\left[\frac{\partial\mu_B}{\partial(1 - x)}\right]_T \qquad \text{(IV.146)}$$

From the definitions of the fugacity and activity of a component in a solution, it is readily seen that

$$x\frac{\partial \ln \bar{f}_A}{\partial x} = (1 - x)\frac{\partial \ln \bar{f}_B}{\partial(1 - x)} \qquad \text{(IV.147)}$$

and
$$x\frac{\partial \ln \bar{a}_A}{\partial x} = (1 - x)\frac{\partial \ln \bar{a}_B}{\partial(1 - x)} \qquad \text{(IV.148)}$$

Equations (IV.146), (IV.147), and (IV.148) are forms of an equation commonly known as the Duhem equation or sometimes as the Duhem-Margules equation. Eq. (IV.148) may also be written in the form

$$d \ln \bar{a}_A = -\frac{1 - x}{x} d \ln \bar{a}_B \qquad \text{(IV.149)}$$

It can readily be shown that

$$d \ln x = -\frac{1 - x}{x} d \ln (1 - x) \qquad \text{(IV.150)}$$

Subtracting Eq. (IV.150) from Eq. (IV.149), one gets

$$d \ln \frac{\bar{a}_A}{x} = -\frac{1 - x}{x} d \ln \frac{\bar{a}_B}{1 - x} \qquad \text{(IV.151)}$$

a form of the Duhem equation that has proved well suited for graphical computations. These equations [Eqs. (IV.144) to (IV.151)] apply to any homogeneous system or phase.

Single-component System.—For such a case, $x'' = x'$ and Eq. (IV.139) reduces to the form[1]

$$(v'' - v') dp = (S'' - S') dT \qquad \text{(IV.152)}$$

or
$$\frac{dp}{dT} = \frac{\lambda}{T \Delta v} \qquad \text{(IV.153)}$$

where λ = latent heat of phase change.

Δv = volume change accompanying the phase change.

This is a very important equation showing how the equilibrium pressure changes with the temperature for any phase equilibrium in a single-component system. For a liquid-vapor equilibrium it is generally known as the Clausius-Clapeyron equation.

It is desirable at this point to digress to show how Eq. (IV.153) can be directly derived in a very simple manner. The total free energy of a mixture of two phases is the sum of the free energies of the individual phases, or

$$F = N'F' + N''F''$$

---

[1] This assumes that the various derivatives approach a finite value as x'' and x' approach unity.

The necessary condition for the two phases to be in equilibrium is

$$d\mathbf{F} = 0 \tag{IV.25}$$

at constant p and T. The only possible change at constant p and T is the transfer of mass from one phase to another. Let dN moles be transferred from phase ['] to phase [''); then the net change in total free energy, $d\mathbf{F}$, is

$$d\mathbf{F} = (F'' - F')\, dN$$

Applying the criterion of equilibrium,

$$F'' = F'$$

Now, as we change the pressure and temperature, the free energies of the two phases must change in such a way as to preserve this equality, or we can write

$$dF'' = dF'$$

but

$$dF = \frac{\partial F}{\partial p}\, dp + \frac{\partial F}{\partial T}\, dT$$

$$= v\, dp - S\, dT$$

$$\therefore v''\, dp - S''\, dT = v'\, dp - S'\, dT$$

which is the same as Eq. (IV.152)

Solution of Constant Composition.—At constant x', Eq. (IV.138) becomes

$$\frac{dp}{dT} = \frac{S'' - S' - (x'' - x')(\partial S'/\partial x')}{v'' - v' - (x'' - x')(\partial v'/\partial x')} \tag{IV.154}$$

or

$$\frac{dp}{dT} = \frac{\Delta H}{T\, \Delta v} \tag{IV.155}$$

ΔH is the differential latent heat of vaporization when ['') denotes a vapor phase.

Δv is the differential volume change.

At low pressures, v' and $\partial v'/\partial x'$ are negligible compared with v'', and the denominator reduces to v''.

If one component is nonvolatile, $x'' = 1$, and the denominator becomes

$$v'' - \left[v' + (1 - x')\, \frac{\partial v'}{\partial x'} \right] = v'' - \bar{v}'$$

Likewise, the numerator becomes

$$S'' - \left[S' + (1 - x')\, \frac{\partial S'}{\partial x'} \right] = S'' - \bar{S}'$$

This is an entropy difference at a given p and T, and hence

$$S'' - \bar{S}' = \frac{H'' - \bar{H}'}{T}$$

and
$$\frac{dp}{dT} = \frac{H'' - \bar{H}'}{T(v'' - \bar{v}')} \qquad (IV.156)$$

This is a special form of the Clausius-Clapeyron equation relating vapor pressure of the solvent, in a solution containing a nonvolatile solute, to the temperature.

Ideal-gas Phase.—For this case,

$$\pi_0'' = \frac{1}{RT} \int_{p^\circ}^{p} v'' \, dp$$

$$= \ln \frac{p}{p^\circ} \qquad (IV.157)$$

and
$$\frac{\partial \pi_0''}{\partial x''} = \frac{1}{RT} \int_{p^\circ}^{p} \frac{\partial v''}{\partial x''} \, dp = 0 \qquad (IV.158)$$

and
$$\frac{\partial^2 \pi_0''}{\partial x''^2} = 0 \qquad (IV.159)$$

Similarly,
$$\pi'' = \ln p \qquad (IV.160)$$

and
$$\frac{\partial \pi''}{\partial x''} = 0 \qquad (IV.161)$$

By differentiation of Eq. (IV.72)

$$\frac{\partial^2 F}{\partial x^2} = RT \left[\frac{\partial^2 \pi_0}{\partial x^2} + \frac{1}{x(1-x)} \right] \qquad (IV.162)$$

which, for this special case, becomes

$$\frac{\partial^2 F''}{\partial x''^2} = \frac{RT}{x''(1 - x'')} \qquad (IV.163)$$

Noting that
$$\frac{\partial v''}{\partial x''} = 0$$

and that v' may be neglected in comparison with v'', and

$$v'' = \frac{RT}{p}$$

Eq. (IV.139) reduces to

$$RT \frac{dp}{p} - \left[S'' - S' - (x'' - x') \frac{\partial S''}{\partial x''} \right] dT - RT \frac{x'' - x'}{x''(1 - x'')} \, dx'' = 0 \qquad (IV.164)$$

If we again assume $x'' = x'$ (single component) Eq. (IV.164) reduces to

$$RTd \ln p = \Delta S \, dT$$

$$= \frac{L}{T} \, dT$$

or
$$\frac{d \ln p}{dT} = \frac{L}{RT^2} \qquad (IV.165)$$

a special form of the Clausius-Clapeyron equation that is very useful.

An analogous equation can be obtained for a solution at constant composition.   Thus, Eq. (IV.138) for the case of ideal gases and constant x' becomes

$$RT \frac{dp}{p} = \left[S'' - S' - (x'' - x') \frac{\partial S'}{\partial x'} \right] dT \qquad \text{(IV.166)}$$

The expression in the brackets $= L/T$ where L is the differential latent heat of vaporization of the liquid solution.

$$\therefore d \ln p = \frac{L}{RT^2} dT$$

For the special case of constant temperature, $dT = 0$ and Eq. (IV.164) reduces to

$$\frac{\partial \ln p}{\partial x''} = \frac{x'' - x'}{x''(1 - x'')} \qquad \text{(IV.167)}$$

This is a special form of the Duhem equation.

From the definition of the partial pressure

$$\bar{p}_A = x''p$$

and

$$\bar{p}_B = (1 - x'')p$$

and

$$\bar{p}_A + \bar{p}_B = p$$

By introducing these relationships into Eq. (IV.167) it can be changed to the following form:

$$\frac{\partial \ln \bar{p}_A}{\partial \ln x'} = \frac{\partial \ln \bar{p}_B}{\partial \ln (1 - x')} \qquad \text{(IV.168)}$$

This equation also follows directly from Eq. (IV.147) since $\bar{f}_i' = \bar{f}_i'' = \bar{p}_i$ when the vapor phase is an ideal gas.

Upon using Eq. (IV.158), Eq. (IV.140) reduces to

$$\frac{x''}{1 - x''} = \frac{x'}{1 - x'} e^{\frac{\partial \pi'}{\partial x'}} \qquad \text{(IV.169)}$$

Introduction of Eqs. (IV.160) and (IV.161) into Eq. (IV.141) reduces it at once to

$$\pi' + \ln (1 - x') - x' \frac{\partial \pi'}{\partial x'} = \ln p + \ln (1 - x'') \qquad \text{(IV.170)}$$

or

$$p(1 - x'') = (1 - x')e^{\pi' - x'\frac{\partial \pi'}{\partial x'}} \qquad \text{(IV.171)}$$

Substituting $(1 - x')/(1 - x'')$ from Eq. (IV.169),

$$px'' = x'e^{\pi' + (1 - x')\frac{\partial \pi'}{\partial x'}} \qquad \text{(IV.172)}$$

Adding Eqs. (IV.171) and (IV.172),

$$px'' + p(1 - x'') = p$$
$$= x'e^{\pi' + (1 - x')\frac{\partial \pi'}{\partial x'}} + (1 - x')e^{\pi' - x'\frac{\partial \pi'}{\partial x'}} \qquad \text{(IV.173)}$$

This equation relates the vapor pressure of a binary solution to the composition of the liquid phase at constant temperature when the vapor may be assumed an ideal gas.

When $x' = 1$, Eq. (IV.173) reduces to

$$p = p_A$$
$$= e^{\pi'_A}$$

where $\pi_{A'}$ is the value of τ' for pure component A in the liquid phase. Likewise, when $x' = 0$,

$$p = p_B$$
$$= e^{\pi'_B}$$

Using these facts, Eq. (IV.173) can be put in the form

$$p = p_A x' e^{\pi' + (1 - x')\frac{\partial \pi'}{\partial x'} - \pi'_A} + p_B(1 - x')e^{\pi' - x'\frac{\partial \pi'}{\partial x'} - \pi'_B} \qquad (IV.174)$$

p_A and p_B are the vapor pressures of the two components at the given temperature.

Ideal Gas in Second Phase and Ideal Solution in First Phase.—For a binary ideal solution, Eq. (IV.118) becomes

$$\frac{\partial v}{\partial x} = \bar{v}_A - \bar{v}_B$$

$$\therefore \frac{\partial \pi}{\partial x} = \frac{1}{RT} \int (\bar{v}_A - \bar{v}_B) \, dp$$

$$\frac{\partial \pi}{\partial x} = \pi_A - \pi_B \qquad (IV.175)$$

and

$$\pi = \pi_A x + \pi_B(1 - x) \qquad (IV.176)$$

Substitution of Eqs. (IV.175) and (IV.176) in Eq. (IV.174) gives

$$p = p_A x' + p_B(1 - x') \qquad (IV.177)$$

Similarly, Eq. (IV.169) becomes

$$\frac{x''}{1 - x''} = \frac{p_A}{p_B} \cdot \frac{x'}{1 - x'} \qquad (IV.178)$$

Eqs. (IV.177) and (IV.178) are simple and useful isothermal relations that may be seen to apply strictly only when the second phase is an ideal gas mixture and the first phase an ideal solution.

Since

$$p = \bar{p}_A + \bar{p}_B$$
$$= px'' + p(1 - x'') \qquad (IV.179)$$

it is evident from Eq. (IV.177) that

$$\bar{p}_A = p_A x' \qquad (IV.180)$$
$$\bar{p}_B = p_B(1 - x') \qquad (IV.181)$$

The relationship expressed by Eq. (IV.180) or (IV.181) is generally known as Raoult's law after the French physicist who discovered it empirically.

Differentiating Eq. (IV.177) with respect to T at constant x' and dividing by p,

$$\frac{1}{p}\frac{dp}{dT} = \frac{x'}{p}\frac{dp_A}{dT} + \frac{1-x'}{p}\frac{dp_B}{dT} \tag{IV.182}$$

but

$$\frac{x'}{p} = \frac{x''}{p_A}$$

and

$$\frac{1-x'}{p} = \frac{1-x''}{p_B}$$

Substituting these two equations in Eq. (IV.182),

$$\frac{1}{p}\frac{dp}{dT} = \frac{x''}{p_A}\frac{dp_A}{dT} + \frac{1-x''}{p_B}\frac{dp_B}{dT} \tag{IV.183}$$

but, by Eq. (IV.165),

$$\frac{1}{p_A}\frac{dp_A}{dT} = \frac{L_A}{RT^2}$$

where L_A is the latent heat of vaporization of pure component A at the temperature of the mixture.

$$\therefore \frac{1}{p}\frac{dp}{dT} = \frac{x''L_A + (1-x'')L_B}{RT^2} \tag{IV.184}$$

For the case of ideal liquid solution and ideal gases, and assuming liquid volumes negligible in comparison to gas volumes, Eq. (IV.138) reduces to

$$RT\frac{dp}{p} - \left[S'' - S' - (x'' - x')\frac{\partial S'}{\partial x'}\right]dT - RT\left[\frac{x'' - x'}{x'(1-x')}\right]dx' = 0 \tag{IV.185}$$

or, at constant x',

$$\frac{1}{p}\frac{dp}{dT} = \frac{S'' - S' - (x'' - x')\dfrac{\partial S'}{\partial x'}}{RT} \tag{IV.186}$$

Comparing Eqs. (IV.184) and (IV.186),

$$x''L_A + (1-x'')L_B = T\left[S'' - S' - (x'' - x')\frac{\partial S'}{\partial x'}\right] \tag{IV.187}$$

$$\therefore \left(\frac{\partial \ln p}{\partial T}\right)_{x'} = \frac{x''L_A + (1-x'')L_B}{RT^2}$$

$$= \frac{L_m}{RT^2} \tag{IV.188}$$

where L_m is the mean latent heat of vaporization of the mixture. This is analogous to Eq. (IV.165) for a single component.

The right-hand member of Eq. (IV.187) has already been shown to be the differential latent heat of vaporization of the liquid phase. In general, the vaporization of a solution can be regarded as consisting of two distinct steps, (1) the separation of the liquids and (2) the vaporization of the pure components. In the general case, both these steps involve a change in heat content, that of step 1 commonly being called the "heat of solution." Since the left-hand member of Eq. (IV.187) involves only the latent heats of the pure components, it is clear that the assumption of ideal gases and ideal solutions requires that there be no heat of solution.

It is to be noted that the Tx' relationship at constant pressure, unlike the px' and pT relationships, does not reduce to any simple form for this case.

Ideal Solutions in Both Phases.—Equation (IV.143) may be written

$$\frac{x''}{x'} = \frac{e^{\bar{\tau}_A'}}{e^{\bar{\tau}_A''}}$$

$$= \frac{e^{\left[\frac{1}{RT}\int \bar{v}_A' dp\right]}}{e^{\left[\frac{1}{RT}\int \bar{v}_A'' dp\right]}} \qquad (IV.143)$$

If component A is stable in the vapor phase at the pressure and temperature of the solution, then $\bar{v}_A'' = v_A''$ for an ideal solution, and

$$e^{\left[\frac{1}{RT}\int v_A'' \, dp\right]} = e^{\bar{\tau}_A''} = f_A''$$

By analogy, we might write $\bar{v}_A' = v_A'$ and

$$e^{\left[\frac{1}{RT}\int v_A' \, dp\right]} = f_A'$$

but this is open to serious objection; for A does not exist in stable equilibrium as a pure liquid at the pressure and temperature of the solution, and so v_A' and likewise f_A' are hypothetical quantities. These assumptions transform Eq. (IV.143) to

$$\frac{x''}{x'} = \frac{f_A'}{f_A''} \qquad (IV.189)$$

where f_A'' and f_A' are, respectively, the fugacity of pure A in the vapor phase and in the liquid phase at the pressure and temperature of the solution. f_A' would have to be obtained by extrapolation into an unstable region.

For an ideal solution, $\bar{v}'_A$ is a constant, and if we assume it to be independent of pressure for moderate pressures Eq. (IV.143) can be written

$$\frac{x''}{x'} = \frac{e^{\frac{k_A p}{RT}}}{f''_A} \tag{IV.190}$$

where k_A is the constant value of $\bar{v}'_A$.

The analogous equations for component B are

$$\frac{1 - x''}{1 - x'} = \frac{f'_B}{f''_B} \tag{IV.191}$$

and

$$\frac{1 - x''}{1 - x'} = \frac{f'_B}{e^{\frac{k_B p}{RT}}} \tag{IV.192}$$

and in this case f''_B is a hypothetical quantity that might be obtained by extrapolation.

Equation (IV.138) for the special case of isothermal conditions and ideal solutions becomes, with the aid of Eq. (IV.111),

$$[x''(\bar{v}''_A - \bar{v}'_A) + (1 - x'')(\bar{v}''_B - \bar{v}'_B)]\,dp = RT\,\frac{x'' - x'}{x'(1 - x')}\,dx' \tag{IV.193}$$

The analogous equation from Eq. (IV.139) is

$$[x'(\bar{v}''_A - \bar{v}'_A) + (1 - x')(\bar{v}''_B - \bar{v}'_B)]\,dp = RT\,\frac{x'' - x'}{x''(1 - x'')}\,dx'' \tag{IV.194}$$

These equations might be regarded as the special forms of the Duhem equation when both the liquid and the vapor solutions are ideal. At this point we shall consider a special case for which Eq. (IV.193) becomes integrable, *viz.*, that of a slightly soluble gas in a solvent that may be considered nonvolatile (for example, nitrogen in water at ordinary temperatures). For this case, $x'' = 1$, and $\bar{v}''_A = v''_A$; and making these substitutions in Eq. (IV.193) one gets

$$(v''_A - \bar{v}'_A)\,dp = RT\,\frac{dx'}{x'} \tag{IV.195}$$

Integrating with the assumption that $\bar{v}'_A$ is independent of p,

$$\int v''_A\,dp - \bar{v}'_A p = RT\ln x' + c \tag{IV.196}$$

or

$$RT\ln f_A - \bar{v}'_A p = RT\ln x' + c \tag{IV.197}$$

When $p = 1$, assume $f = p$; then $f_A = 1$, and $x' = x'_1$, the solubility at 1 atm. total pressure. Making the proper substitutions in Eq. (IV.197),

$$\ln x' = \ln x'_1 + \ln f_A + \frac{\bar{v}'_A}{RT}\,(1 - p) \tag{IV.198}$$

or

$$x' = x'_1 f_A e^{\left[\frac{\bar{v}'_A}{RT}(1 - p)\right]} \tag{IV.199}$$

If the exponent were zero, Eq. (IV.199) would become

$$x' = x_1' f_A$$

or

$$x' = k f_A \qquad \text{(IV.200)}$$

an equation analogous to the usual form of Henry's law, but with the pressure replaced by the fugacity. Such an equation is not in accord with the data on actual systems whereas Eq. (IV.199) has been shown to apply quite well.

One other special case of interest is that of a condensed phase which is volatile, subjected to pressure by a gas which can be regarded as insoluble, for example, a liquid like water or a solid like $BaCl_2 \cdot 8NH_3$ subjected to hydrogen pressure. If x refers to the mole fraction of the inert gas, $x' = 0$ and $\bar{v}_B' = v_B'$ and Eq. (IV.194) reduces to

$$(\bar{v}_B'' - v_B')\, dp = -RT\, \frac{d(1 - x'')}{1 - x''} \qquad \text{(IV.201)}$$

This is a relatively simple relation between the mole fraction of the less volatile component (the water or ammonia, for example) in the gas phase and the pressure.

For the case of ideal solutions, Eq. (IV.140) becomes

$$\frac{x''}{1 - x''} = \frac{x'}{1 - x'}\, e^{\frac{1}{RT}\left[\int (\bar{v}_A' - \bar{v}_B')dp - (\bar{v}_A'' - \bar{v}_B'')dp\right]} \qquad \text{(IV.202)}$$

The quantities $\bar{v}$ are independent of x, and $\bar{v}'$ might be regarded as independent of p also, at least to moderate pressures.

Applying the assumption of ideal solutions to Eq. (IV.126) gives

$$RT\, \frac{dx'}{x'} + \bar{v}_A'\, dp - \bar{S}_A'\, dT = RT\, \frac{dx''}{x''} + \bar{v}_A''\, dp - \bar{S}_A''\, dT \qquad \text{(IV.203)}$$

At constant pressure, we can write

$$\frac{dx''}{x''} - \frac{dx'}{x'} = \frac{\bar{S}_A'' - \bar{S}_A'}{RT}\, dT \qquad \text{(IV.204)}$$

$$\frac{dx''}{x''} - \frac{dx'}{x'} = \frac{\bar{H}_A'' - \bar{H}_A'}{RT^2}\, dT \qquad \text{(IV.205)}$$

or

$$\left[\frac{\partial \ln (x''/x')}{\partial T}\right]_p = \frac{\bar{H}_A'' - \bar{H}_A'}{RT^2} \qquad \text{(IV.206)}$$

Writing x''/x as an equilibrium constant K and writing $\bar{H}_A'' - \bar{H}_A'$ as $\Delta \bar{H}_A$, we obtain

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta \bar{H}_A}{RT^2} \qquad \text{(IV 207)}$$

If we assume that $\Delta \bar{H}_A$ is a constant independent of T (the assumption

of ideal solution already implies it is independent of x) Eq. (IV.207) may be integrated to

$$\ln \frac{K_2}{K_1} = \frac{\Delta \bar{H}_A}{R} \frac{T_2 - T_1}{T_1 T_2} \qquad \text{(IV.208)}$$

This equation is useful for calculation of heat of solution from solubility data. In the special case where one phase consists of nearly pure component A—for example, the solubility of a gas like CO_2 in water—the equation becomes

$$\ln \frac{x_2}{x_1} = \frac{\Delta \bar{H}_A}{R} \frac{T_2 - T_1}{T_1 T_2} \qquad \text{(IV.209)}$$

where x_2 and x_1 are the concentrations of gas in the liquid solution at the two temperatures.

Equation (IV.207) is analogous to the van't Hoff equation for the change of a chemical equilibrium constant with temperature or to the Clausius-Clapeyron equation for vapor pressure as a function of temperature.

Dilute Solutions.—The term "dilute solution" is, of course, an indefinite one, and no exact definition can be given. For most purposes we might think of it as meaning a solution in which one of the components of a binary system is present to the extent of 5 mole per cent or less. The so-called "laws of dilute solutions" are limiting laws for the case where the mole fraction approaches zero or unity. As the mole fraction of a solute increases from the limiting value of zero, the limiting laws will become less and less accurate. These laws are generally quite simple, and in many cases it may be convenient to use them as approximations up to relatively high concentrations. Obviously, the degree of departure from these laws will depend on circumstances, and no general statement governing it can be made.

Case I: *Vapor Is an Ideal Gas.*—As x approaches 1 or 0, the term $1/x(1 - x)$ of Eq. (IV.162) becomes very large whereas $\partial^2 \pi/\partial x^2$ remains a small quantity. (Note that $\partial^2 \pi/\partial x^2$ is related to the deviation from ideal solution and is therefore never a large figure. For an ideal solution it equals 0.) Also, $\partial v''/\partial x'' = 0$ since the vapor is an ideal gas. These special conditions plus the assumption that liquid volumes are negligible compared with vapor volumes, reduce Eqs. (IV.138) and (IV.139), respectively, to

$$RT \frac{dp}{p} - L \frac{dT}{T} - RT \frac{x'' - x'}{x'(1 - x')} dx' = 0 \qquad \text{(IV.210)}$$

$$RT \frac{dp}{p} - L \frac{dT}{T} - RT \frac{x'' - x'}{x''(1 - x'')} dx'' = 0 \qquad \text{(IV.211)}$$

where L is the latent heat of vaporization of the pure solvent (*i.e.*, the component whose mole fraction approaches 1).

At constant temperature,

$$\frac{dp}{p} = \frac{x'' - x'}{x'(1 - x')} dx' \qquad \text{(IV.212)}$$

$$\frac{dp}{p} = \frac{x'' - x'}{x''(1 - x'')} dx'' \qquad \text{(IV.213)}$$

or

$$\frac{dx'}{x'(1 - x')} = \frac{dx''}{x''(1 - x'')} \qquad \text{(IV.214)}$$

Integration yields the relation

$$\frac{x''}{1 - x''} = k \frac{x'}{1 - x'} \qquad \text{(IV.215)}$$

where k is an empirical constant for a given temperature.

Substituting the value of x'' given by Eq. (IV.215) into Eq. (IV.213), one arrives at the equation

$$\frac{dp}{p} = \frac{(k - 1) \, dx'}{1 + (k - 1)x'} \qquad \text{(IV.216)}$$

Integration of Eq. (IV.216) gives

$$\ln p = \ln [1 + (k - 1)x'] + c \qquad \text{(IV.217)}$$

When $x' = 0$, $p = p_B$. Substituting these boundary conditions and eliminating k by Eq. (IV.215),

$$p(1 - x'') = p_B(1 - x') \qquad \text{(IV.218)}$$

This is Raoult's law again, and we see that it applies only to the *solvent* in a dilute solution of liquids when the vapor is an ideal gas. With the boundary conditions $x' = 1$, $p = p_A$, one gets the analogous equation for component A.

From Eqs. (IV.215) and (IV.218) we get

$$px'' = kp_B x' = cx' \qquad \text{(IV.219)}$$

or the partial pressure of the solute is proportional to its mole fraction, but the proportionality constant in this case is a purely empirical one. This relationship is commonly called Henry's law from the English scientist who discovered it empirically from the results of studies on the solubility of gases in liquids.

The same equation for the case of a dilute solution of a noncon densable gas may be very simply obtained from Eq. (IV.212) by putting $x'' = 1$ (*i.e.*, neglecting the vapor of the liquid solvent in the gas phase). Thus, we have

$$\frac{dp}{p} = \frac{dx'}{x'}$$

or

$$x' = cp \qquad \text{(IV.220)}$$

where c is a Henry's law constant.

For the case of a dilute solution of a nonvolatile solute in a volatile solvent, x'' (mole fraction of solute) $= 0$, and Eq. (IV.212) becomes

$$\frac{dp}{p} = -\frac{dx'}{1-x'}$$
$$= \frac{d(1-x')}{(1-x')}$$

Integrating and inserting the boundary condition: $x' = 0$, $p = p_B$,

$$x' = 1 - (p/p_B),$$

or

$$x' = \frac{p_B - p}{p_B} \tag{IV.221}$$

This is Raoult's law of vapor-pressure lowering and is the same as Eq. (IV.218) for the case where $x'' = 0$.

Returning to the general dilute-solution equations (IV.210) and (IV.212) and taking the special case of constant pressure, it is evident that Eq. (IV.215) also applies to this case.

At constant pressure, Eq. (IV.210) becomes

$$\frac{L}{RT^2}\,dT = \frac{x''-x'}{x'(1-x')}\,dx' \tag{IV.222}$$

Substituting for x'' its value from Eq. (IV.215),

$$\frac{L}{RT^2}\,dT = \frac{k-1}{1+(k-1)x'}\,dx' \tag{IV.223}$$

Integrating on the assumption of constant L and inserting the boundary condition $T = T_B$ (boiling point of pure solvent) when $x' = 0$, one has

$$\frac{L}{R}\left(\frac{1}{T} - \frac{1}{T_B}\right) = \ln\left[1 + (k-1)x'\right] \tag{IV.224}$$

When x' is small, $\ln\left[1 + (k-1)x'\right]$ can be shown, by expanding it, to approach the value $(k-1)x'$. Therefore, Eq. (IV.224) can be written

$$\frac{1}{T} - \frac{1}{T_B} = \frac{R}{L}(k-1)x'$$

or

$$T_B - T = \frac{RTT_B}{L}(k-1)x' \tag{IV.225}$$

or, putting $T = T_B$ as a justifiable approximation in the expression on the right-hand side of the equation,

$$T - T_B = c\frac{RT_B^2}{L}x' \tag{IV.226}$$

where c is an empirical constant. This is a law of boiling-point change

(may be either a lowering or a raising, depending on which component is the one present in low concentration) for a volatile solute in a volatile solvent).

If the solute is nonvolatile, $x'' = 0$, and Eq. (IV.222) becomes

$$-\frac{L}{RT^2}\,dT = \frac{d(1 - x')}{(1 - x')} \tag{IV.227}$$

Integrating and inserting boundary conditions,

$$\frac{L}{R}\left(\frac{1}{T} - \frac{1}{T_B}\right) = \ln\,(1 - x') \tag{IV.228}$$

or, when x' is small compared with 1,

$$T - T_B = \frac{RT_B^2}{L}\,x' \tag{IV.229}$$

This is the usual equation given for the boiling-point raising of a dilute solution of a nonvolatile solute.

The general equations apply just as well to solid-liquid or solid-gas equilibria as to liquid-gas equilibria. For example, assume that phase ['] is a solid phase and that pure solid B separates from the liquid phase (case of mixtures that form a eutectic); then x'' in Eq. (IV.222) $= 0$, and L is now the latent heat of melting of pure B. In this way we obtain the equation for freezing-point lowering,

$$T - T_F = \frac{RT_F^2}{L}\,x' \tag{IV.230}$$

where T_F = freezing point of pure B at the given pressure. T = freezing point of the solution.[1]

Case II: *Vapor Is Not an Ideal Gas.*—For the case of constant temperature, Eqs. (IV.138 and (IV.139) become, respectively,

$$\left[v'' - v' - (x'' - x')\frac{\partial v'}{\partial x'}\right]dp = RT\,\frac{x'' - x'}{x'(1 - x')}\,dx' \tag{IV.231}$$

and $\left[v'' - v' - (x'' - x')\dfrac{\partial v''}{\partial x''}\right]dp = RT\,\dfrac{x'' - x'}{x''(1 - x'')}\,dx'' \tag{IV.232}$

For the special case of volatile solute in substantially nonvolatile solvent, $x' \to 0$, $x'' \to 1$, $v'' \to v_A''$, and $v' \to v_B'$. Furthermore, $\partial v'/\partial x'$ may be considered constant over the short range of x' in question. With these substitutions, Eq. (IV.231) becomes

$$(v_A'' - v_B' - c)\,dp = RT\,\frac{dx'}{x'} \tag{IV.233}$$

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[1] This, of course, does not come under the case of the vapor being an ideal gas. As a matter of fact, Eq. (IV.222) from which Eq. (IV.230) was derived is true whether or not the phase ['] is an ideal gas.

where $c = \partial v'/\partial x'$. Letting $v'_B + c = k$ and proceeding as in the case of Eq. (IV.195), we arrive at

$$x' = x'_1 f_A e^{\frac{k}{RT}(1-p)} \tag{IV.234}$$

This is substantially the same as Eq. (IV.199).

The Poynting Relation.—Imagine a two-phase system at constant composition and constant temperature but with a different pressure on each phase. For such a case Eq. (IV.126) becomes

$$\bar{v}'_A \, dp' = \bar{v}''_A \, dp'' \tag{IV.235}$$

or, if the two phases are single-component,

$$v' \, dp' = v'' \, dp'' \tag{IV.236}$$

This equation has been used to calculate the effect of pressure on the vapor pressure of a solid or a liquid. This involves the assumption of a semipermeable membrane to maintain different pressures on the two phases. Actually, this effect, known as the Poynting effect from its discoverer, is never obtained alone but is always obscured by other effects because the only practical means of increasing the total pressure on a condensed phase in equilibrium with its vapor is to use a gas and this is never entirely inert. It dissolves in the condensed phase and also exerts an attractive force on the molecules of vapor.

CHEMICAL EQUILIBRIUM

The Equilibrium Constant.—Consider the following general reaction to take place in a given phase, either liquid or gaseous,

$$aA + bB + \cdots = lL + mM + \cdots \tag{IV.237}$$
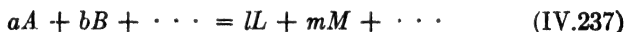
where $a, b, \ldots$ represent the stoichiometric numbers of the reactants $A, B, \ldots$ and $l, m, \ldots$ the corresponding numbers for the products $L, M, \ldots$; and assume that sufficient time has been allowed so that a state approaching equilibrium has been reached. Equation (IV.32) expresses the general condition for any homogeneous equilibrium at constant pressure and temperature, and for this special case it may be written

$$-\mu_A \, dN_A - \mu_B \, dN_B - \cdots + \mu_L \, dN_L + \mu_M \, dN_M + \cdots = 0 \tag{IV.238}$$

the minus sign signifying that, as the reaction proceeds from left to right, the amounts of A, B, etc., decrease and of L, M, etc., increase. It is purely a convention which side of the equation shall be considered reactants and therefore decreasing in amount. Since we are dealing with a true equilibrium, the reaction is reversible and at the equilibrium point can be made to proceed in either direction with just the slightest shift in external conditions.

From the stoichiometric relationships we have the equations

$$\frac{dN_A}{dN_B} = \frac{a}{b}; \qquad \frac{dN_A}{dN_L} = \frac{a}{l}; \text{ etc.}$$

Then Eq. (IV.238) can be put in the form

$$-a\mu_A - b\mu_B - \cdots + l\mu_L + m\mu_M + \cdots = 0 \qquad \text{(IV.239)}$$

Introducing Eq. (IV.38) into (IV.239),

$$-a(RT \ln \bar{a}_A + \mu_A^\circ) - b(RT \ln \bar{a}_B + \mu_B^\circ) - \cdots + l(RT \ln \bar{a}_L + \mu_L^\circ) \\ + m(RT \ln \bar{a}_M + \mu_M^\circ) + \cdots = 0 \qquad \text{(IV.240)}$$

This is readily transformed to

$$\frac{(\bar{a}_L)^l(\bar{a}_M)^m \cdots}{(\bar{a}_A)^a(\bar{a}_B)^b \cdots} = e^{-\frac{\Delta\mu^\circ}{RT}} \qquad \text{(IV.241)}$$

where $\qquad \Delta\mu^\circ = l\mu_L^\circ + m\mu_M^\circ + \cdots - a\mu_A^\circ - b\mu_B^\circ - \cdots \qquad$ (IV.242)

Since μ° is based on a definite state of pressure and concentration, the quantity on the right-hand side of Eq. (IV.241) is a function of temperature only and is commonly called an "equilibrium constant." Thus,

$$e^{-\frac{\Delta\mu^\circ}{RT}} = K_a \qquad \text{(IV.243)}$$

or $\qquad\qquad\qquad \Delta\mu^\circ = -RT \ln K_a \qquad\qquad\qquad$ (IV.244)

If the standard state for each component is the pure substance, Eq. (IV.244) becomes

$$\Delta F^\circ = -RT \ln K_a \qquad \text{(IV.245)}$$

Following the common custom, we shall use Eq. (IV.245) in all cases even though Eq. (IV.244) would be more strictly correct in some.

In deriving Eq. (IV.241) we assumed a homogeneous reaction, but this restriction is readily removed and the equation made applicable to any chemical equilibrium regardless of the phases present. In a chemically reacting system containing solid and liquid phases as well as a gas phase, it is clear that when the whole system is in equilibrium we must have chemical equilibrium in the gas phase and phase equilibrium between the various phases. In other words, we can treat any reaction as a homogeneous gas-phase equilibrium since all substances can be regarded as having some vapor pressure. Furthermore, for equilibrium between the phases we have the equations

$$\mu_i' = \mu_i'' = \mu_i''' = \cdots$$

and $\qquad\qquad RT \ln a_i' = RT \ln a_i'' + c_i^\circ \qquad\qquad$ (IV.246)

where c_i° is a constant depending on the choice of standard states. $\quad c_i^\circ = 0$

if the standard state of the component is the same regardless of phase. In other words, the activities of a given component in the various phases are either equal or proportional.

Therefore, in Eq. (IV.241) the activity can be that in any phase, and the equation is a general mass-action relationship for any chemical equilibrium. Since the numerical value of the equilibrium constant depends on the choice of standard states, one must be careful when using the equation to calculate activities or related quantities, to be sure that no change in standard state has been made.

Since
$$a = \frac{f}{f^\circ}$$

and, for a gas,
$$f^\circ = p^\circ$$

we can write Eq. (IV.241) for a gaseous equilibrium in the form

$$\frac{(f_L)^l (f_M)^m \cdots}{(f_A)^a (f_B)^b \cdots} = (p^\circ)^{\Sigma n} e^{-\frac{\Delta F^\circ}{RT}} = K_f \qquad \text{(IV.247)}$$

For practical purposes p° is taken as 1 atm. and $(p^\circ)^{\Sigma n} = 1$. The equilibrium constant in Eq. (IV.247) is sometimes represented by the symbol K_{p°.

Ideal Gases.—Equation (IV.86) reduces for the case of an ideal gas to

$$f_i = p x_i \qquad \text{(IV.248)}$$

Substituting in Eq. (IV.247), we have

$$\frac{(x_L p)^l (x_M p)^m \cdots}{(x_A p)^a (x_B p)^b \cdots} = K_{p^\circ} \qquad \text{(IV.249)}$$

This is the form in which the law of mass action has been most commonly used. From its derivation it is apparent that it is only a limiting case which the more general law approaches as the pressure approaches zero.

Ideal Solution.—For such a solution we have previously shown that $a_i = x_i$ when the standard state is that of the pure component at the pressure and temperature of the solution. Applying this to liquid solutions, Eq. (IV.249) becomes

$$\frac{(x_L)^l (x_M)^m \cdots}{(x_A)^a (x_B)^b \cdots} = e^{-\frac{\Delta F^\circ}{RT}} = K_x \qquad \text{(IV.250)}$$

For the case of gaseous solutions, combination of Eqs. (IV.247) and (IV.115) gives

$$\frac{(x_L f_L)^l (x_M f_M)^m \cdots}{(x_A f_A)^a (x_B f_B)^b \cdots} = K_f \qquad \text{(IV.251)}$$

This can also be written,

$$\frac{(x_L)^l (x_M)^m \cdots}{(x_A)^a (x_B)^b \cdots} = K_f \left[\frac{(f_A)^a \cdot (f_B)^b \cdots}{(f_L)^l \cdot (f_M)^m \cdots} \right] = K_x \qquad \text{(IV.252)}$$

K_x is an equilibrium constant that is a function of both pressure and temperature but independent of the composition.

Definition of K_p and K_γ.—Let us define a function K_p by the equation

$$\frac{(x_L p)^l (x_M p)^m \cdots}{(x_A p)^a (x_B p)^b \cdots} = K_p \tag{IV.253}$$

K_p is not truly an equilibrium "constant" because it is clearly a function of temperature, pressure, and composition, as can be seen by comparing this equation with Eq. (IV.247) and noting that K_f is a function of temperature only. As the pressure is reduced and approaches zero as a limit, K_p approaches K_{p° or K_f as a limiting value. Combining Eqs. (IV.251) and (IV.253),

$$\frac{K_f}{K_p} = \frac{(\gamma_L)^l (\gamma_M)^m \cdots}{(\gamma_A)^a (\gamma_B)^b \cdots} = K_\gamma \tag{IV.254}$$

$\gamma_i = f_i/p$ and is sometimes called the activity (or fugacity) coefficient. K_γ is a function of pressure and temperature but not of composition.

Effect of Temperature on the Equilibrium Constant.—From Eq. (IV.243),

$$\ln K_a = -\frac{\Delta\mu^\circ}{RT}$$

Differentiating with respect to temperature,

$$\frac{d \ln K_a}{dT} = \frac{\Delta\mu^\circ}{RT^2} - \frac{1}{RT} \frac{d(\Delta\mu^\circ)}{dT} \tag{IV.255}$$

It should be noted that these are not partial derivatives at constant p and x as sometimes written, because K_a is a function of T only. By Eq. (IV.100),

$$\frac{d\mu_i^\circ}{dT} = -\bar{S}_i^\circ$$

and

$$\frac{d(\Delta\mu^\circ)}{dT} = -\Delta\bar{S}^\circ \tag{IV.256}$$

Furthermore, from the definition of F and μ,

$$\mu_i^\circ = \bar{H}_i^\circ - T\bar{S}_i^\circ$$

and

$$\Delta\mu^\circ = \Delta\bar{H}^\circ - T \Delta\bar{S}^\circ \tag{IV.257}$$

Substituting Eqs. (IV.256) and (IV.257) in (IV.255),

$$\frac{d \ln K_a}{dT} = \frac{\Delta\bar{H}^\circ}{RT^2} \tag{IV.258}$$

where $\quad \Delta\bar{H}^\circ = l\bar{H}_L^\circ + m\bar{H}_M^\circ + \cdots - a\bar{H}_A^\circ - b\bar{H}_B^\circ - \cdots \tag{IV.259}$

$\bar{H}_i^\circ$ is the partial molal enthalpy of any component taking part in the

reaction at the particular standard state of pressure and composition chosen.   It is a function only of the temperature.

When the standard state of each component is taken as the pure substance, Eqs. (IV.258) and (IV.259) become

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{IV.260}$$

and $$\Delta H^\circ = lH_L^\circ + mH_M^\circ + \cdots - aH_A^\circ - bH_B^\circ - \cdots \tag{IV.261}$$

GENERALIZED FORCES

In all our derivations of this chapter and the previous one, it was assumed that a uniform fluid pressure p was the only force acting.   In other words, we ruled out all such forces as surface tension, gravity, electrostatic forces, magnetic forces, and e.m.fs.   There are some important cases, particularly in the field of electrochemistry, where we wish to include the effect of other forces, and we shall therefore conclude this chapter with a very brief discussion of the general procedure when such other forces are to be considered.

The first and second laws of thermodynamics applied to any closed system at equilibrium led to the equation

$$T \, dS = dE + dW \tag{IV.262}$$

and, when p was the only force,

$$T \, dS = dE + p \, dv$$

Now let us assume that ζ represents any generalized force or intensity factor and X the corresponding generalized displacement or capacity factor; then Eq. (IV.262) becomes

$$T \, dS = dE + p \, dv + \zeta \, dX \tag{IV.263}$$

With this equation as a starting point, many of the equations developed in Chap. III can be generalized to include the effect of the force ζ.   For example,

$$F = E - TS + pv$$

by definition of the function free energy.   Differentiating and comparing with Eq. (IV.263),

$$dF = -S \, dT + v \, dp + \zeta \, dX \tag{IV.264}$$

and $$S = -\left(\frac{\partial F}{\partial T}\right)_{p,X}$$

and $$\zeta = \left(\frac{\partial F}{\partial X}\right)_{p,T}$$

Likewise, $$F = H + T\left(\frac{\partial F}{\partial T}\right)_{p,X} \tag{IV.265}$$

This equation has important applications in electrochemistry.

At constant pressure,

$$dF = -S\,dT + \zeta\,dX$$

and then
$$-\left(\frac{\partial S}{\partial X}\right)_{p,T} = \left(\frac{\partial \zeta}{\partial T}\right)_{p,X} \tag{IV.266}$$

For some applications, it becomes desirable to generalize the definition of some of our functions to include the generalized force and displacement. For example, let us redefine F by the equation

$$F = E - TS + pv + \zeta X \tag{IV.267}$$

Then
$$dF = v\,dp - S\,dT + X\,d\zeta \tag{IV.268}$$

From this we obtain

$$\left(\frac{\partial X}{\partial T}\right)_{p,\zeta} = -\left(\frac{\partial S}{\partial \zeta}\right)_{p\,T} \tag{IV.269}$$

Applying this to a substance in a magnetic field, $\zeta = -H$, the magnetic-field strength, and $X = I$, the intensity of magnetization, and hence

$$\left(\frac{\partial I}{\partial T}\right)_{p,H} = \left(\frac{\partial S}{\partial H}\right)_{p,T} \tag{IV.270}$$

Magnetic susceptibility χ (analogous to electrical conductance) is defined by the equation

$$\chi = \frac{I}{H}$$

At constant H,
$$dI = H\,d\chi$$

Combining this with Eq. (IV.270),

$$\left(\frac{\partial S}{\partial H}\right)_{p,T} = H\left(\frac{\partial \chi}{\partial T}\right)_{p,H} \tag{IV.271}$$

This equation has important applications to the production of very low temperatures in the region close to absolute zero. For further details, reference should be made to an interesting paper by Giauque.[1]

[1] GIAUQUE, W. F., *Ind. Eng. Chem.*, **28,** 743 (1936).

CHAPTER V

PRESSURE-VOLUME-TEMPERATURE RELATIONSHIPS OF FLUIDS

The calculation of the thermodynamic properties of any fluid by means of the equations developed in Chaps. III and IV requires some knowledge of the pvT behavior of the fluid to permit the integration of the differential equations relating the property to the variables of state. Furthermore, such data are essential in many important engineering problems such as the determination of size of gas storage vessels, calculation of pressure drop due to fluid flow, metering the flow of gases, and determining times of contact in reaction vessels. It is the purpose of this chapter to review and summarize our knowledge of the way in which the volume (or the density) of fluids changes with the temperature, the pressure, and in the case of solutions, the composition. The discussion will be confined to gases, the data on liquids being much less extensive and of lesser importance. The first part of the treatment of this subject will deal entirely with pure gases, but later an extension to gas mixtures will be made. The relationships may be presented in graphical form or in the form of an equation. An equation that represents the pvT behavior of a fluid is generally called an "equation of state." This is a convenient way of condensing a large amount of data and putting them in a form that is useful for various applications.

THE IDEAL GAS

The early investigations of the behavior of gases led to the two simple laws

$$pV = k_1 \qquad \text{(Boyle's law)} \qquad \text{(V.1)}$$

and
$$V = k_2 T \qquad \text{(Charles's law)} \qquad \text{(V.2)}$$

where k = a constant at a given temperature. k_2 = a constant for a given pressure.[1]

Combination of these two equations leads to the relation

$$pV = kT \qquad \text{(V.3)}$$

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[1] It should be noted that Charles's law in this form is bound up with the question of the definition of the temperature scale. All it really does is to define a temperature on a constant-pressure gas-thermometer scale. For an ideal gas the scale so defined has been shown to be identical with the thermodynamic scale, which was defined in Chap. III; all our discussion will be based on this scale unless otherwise noted.

k depends on the units, on the mass, and on the nature of the gas in question; but if we choose one mole of gas in all cases, then k becomes a universal constant independent of the nature of the gas and dependent only on the units chosen for p, V, and T. Thus we have the familiar equation

$$pv = RT \tag{V.4}$$

or, for any amount of gas,

$$pV = NRT \tag{V.5}$$

$$pV = \frac{m}{M} RT \tag{V.6}$$

It was soon found that the simple behavior required by Eq. (V.5) was only an approximation to the actual behavior of gases. At high densities the deviations from the simple law may be very great; in general, the lower the density, the more closely do actual gases approach this type of behavior. In other words, Eq. (V.5) represents a limiting case that all gases approach as their pressure is lowered or their temperature increased. This leads to the concept of an ideal or perfect gas whose behavior is exactly represented by Eq. (V.5). This concept is of great practical utility because of the simplicity of the equations involved and because of the fact that it represents the behavior of actual gases with sufficient accuracy for practical purposes under a wide variety of conditions. It should, however, be clearly understood that it is only a limiting condition which *all* actual gases may approach more or less closely but never really attain.

From a kinetic standpoint, an ideal gas is one in which the molecules are so small relative to the spaces between them that their own volume is entirely negligible and in which there are no forces of attraction or repulsion between molecules. From such a simple picture and with the aid of the kinetic theory, the ideal-gas equation of state may be derived. Since we are primarily interested in the application of the ideal-gas law rather than its theoretical implications, this question will not be pursued further.

From a thermodynamic standpoint, the ideal gas can be defined in any one of three ways, as follows:

1. By Eq. (V.5).

2. By a statement of Boyle's law and of Joule's law. The latter law states that the energy of a gas is independent of its pressure or its volume, or is a function of temperature only. Stating this mathematically,

$$\left(\frac{\partial E}{\partial v}\right)_T = 0 \tag{V.7}$$

Since the pressure is a dependent variable during a volume change at constant temperature, this equation also implies that the energy is

independent of the pressure.   In general, as we have seen in Chap. III, the energy of a gas depends on two independent variables, for example, the volume and the temperature.   From the simple kinetic picture of an ideal gas, it can be seen that, since there are no forces acting between the molecules, a change in volume alone would not produce any change in the energy content.

3. By Boyle's law and the statement that the **gas shows a zero Joule-Thomson effect**.

The Joule-Thomson effect will be treated more fully in Chap. VII; for our present purpose it is sufficient to state that it is the temperature change resulting from a gas expansion between two *constant* pressures when no external work other than that to maintain the constant pressures is done and when any kinetic-energy effects, temporarily generated, have been dissipated.   An expansion of this type is called a Joule-Thomson expansion, after the two physicists who first employed it in the study of gases.   As will be shown later, the function H remains constant during a Joule-Thomson expansion.   Consequently, the change in temperature with pressure during such an expansion is represented by the coefficient $(\partial T/\partial p)_H$.   By a zero Joule-Thomson effect is meant that

$$\left(\frac{\partial T}{\partial p}\right)_H = 0 \qquad (V.8)$$

at all pressures and temperatures.   For all real gases this coefficient is not zero except at a limited number of points (see Chap. VII) but will be positive or negative depending on circumstances.

That Boyle's law and Joule's law are sufficient to define an ideal gas may be shown as follows:

$$\left(\frac{\partial E}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \qquad (III.78)$$

and therefore, when Joule's law applies,

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = 0 \qquad (V.9)$$

or $$T\,dp - p\,dT = 0 \text{ (at constant volume) } (V.10)$$

or $$\frac{dp}{p} = \frac{dT}{T} \qquad (V.11)$$

Integrating, $$p = kT \qquad (V.12)$$

where the constant k is a function of volume.   Combination of Eqs. (V.12) and (V.1) leads at once to the ideal-gas equation of state in the form given by Eq. (V.3).

Similarly, in the case of the Joule-Thomson effect, we have

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{C_p} \tag{III.97}$$

and, by operations analogous to those just used, we arrive at the equation

$$v = kT \tag{V.13}$$

where k is a function of pressure only. This equation also combines with Eq. (V.1) to give the ideal-gas equation of state. In other words, we have shown that all the three definitions of an ideal gas are equivalent.

When volume is expressed in cubic feet, pressure in pounds per square inch, and temperature in degrees Rankine or Fahrenheit absolute, and mass in pound-moles, then, by Eq. (V.5),

$$\begin{aligned} R &= \frac{pV}{NT} \\ &= \frac{14.70 \times 359.0}{1 \times 491.7} \\ &= 10.735 \end{aligned}$$

The volume occupied by 1 lb.-mole of an ideal gas at the standard conditions of 14.70 lb. per sq. in. and 32°F. or 491.7°R. is 359 cu. ft. Employing the first law of thermodynamics, the pv product can also be expressed in other than mechanical units since it has the dimensions of energy. Thus we may express pv in B.t.u. per pound-mole, and R in B.t.u. per pound-mole per degree Rankine would be

$$\frac{14.7 \times 144 \times 359}{778 \times 491.7} = 1.987$$

Values of R in other units are given in the Appendix.

BEHAVIOR OF REAL GASES

The molecules of real (as distinct from ideal) gases occupy a certain definite volume that may or may not be negligible in comparison with the total volume occupied by the gas; furthermore, they possess fields of force resulting in attractive forces between them. Both these conditions lead to the fact that as the molecules of a gas approach one another (or as the gas becomes denser) the gas departs more and more from the ideal state. If the temperature of the gas is below a certain temperature known as the "critical temperature," an increase in pressure will eventually lead to a condensation of the gas to a liquid. Above the critical temperature a gas can be compressed indefinitely without causing the appearance of another phase. In this way, some gases have been brought

to densities that are higher than the normal density of the liquid or even the solid. For example, Bridgman[1] compressed hydrogen at 65°C. and about 15,000 a^{t}m. to a density of 0.1301 g. per cc. The normal density of the liquid is about 0.071 and that of the solid 0.081. Similar relative values were obtained for nitrogen. It is also of interest to note that, at this pressure and temperature, the volume of nitrogen is sixteen times as great as it would be if it were an ideal gas.

The critical point is a unique point of pressure, temperature, and volume at which the liquid and gas phases are identical. Above the critical temperature only one phase is possible. All gases possess a definite critical point that can be determined experimentally. This point is of considerable practical as well as theoretical importance, and we shall have frequent occasion to refer to it.

In a few cases, unusually large deviations from the ideal-gas laws occur even at relatively low pressures. These are thought to be due to chemical changes resulting in association or dissociation of molecules. Two classic examples are the case of acetic acid and nitrogen peroxide, where the following reactions occur:

$$2 \ CH_3COOH = (CH_3COOH)_2$$
$$2 \ NO_2 = N_2O_4$$
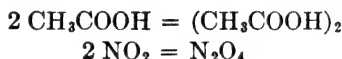
In the case of acetic acid, at 118°C. and 0.94 atm. pressure, the volume calculated from the ideal-gas law on the basis of a molecular weight of 60.03 is 1.65 times the observed volume.

Compressibility Factors.—The behavior of any actual gas has frequently been represented on a plane diagram by plotting the volume vs. the pressure with temperature as parameter. A much more convenient method of representing the behavior is by means of a graph of compressibility factor vs. pressure with temperature as parameter. The compressibility factor that we shall use is defined by the equation

$$C = \frac{pv}{RT} \qquad (V.14)$$

C has the value of unity for any ideal gas under all conditions, and therefore such a plot shows at once the extent of the deviation of the gas from the ideal state, at any condition of pressure and temperature. Equation (V.14) combined with an expression giving C as a function of pressure and temperature for a particular gas would be an equation of state for that gas. The relationship between C and the pressure and temperature is usually given in graphical form. Such a graph for nitrogen gas is given in Fig. V.1. Similar graphs may be prepared, using the other pairs of

[1] BRIDGMAN, P. W., "The Physics of High Pressure," the Macmillan Company, New York, 1931.

independent variables, *viz.*, T, v and p, v. The choice of graph depends on what conditions are given; for example, if the volume is to be determined, given the pressure, temperature, and mass, Fig. V.1 can be used to get C directly, and from Eq. (V.14) one calculates v, the molal volume, and then the total volume from

$$V = Nv$$

If one wishes to calculate the pressure, given the mass, total volume, and
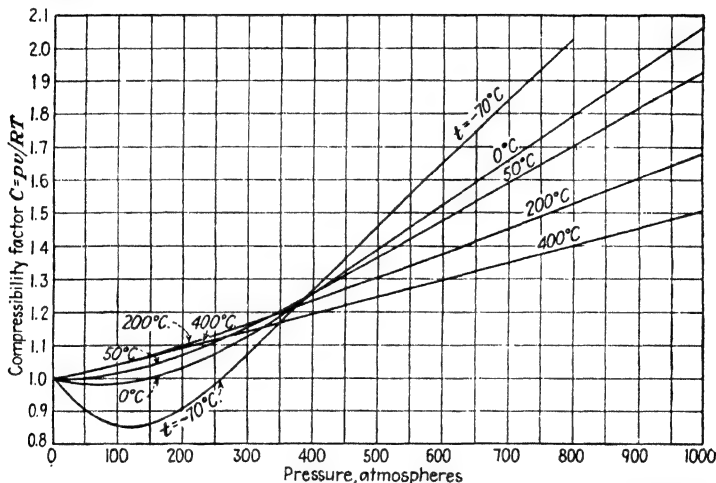
FIG. V.1.—Compressibility factors of nitrogen gas. *Data of E. P. Bartlett, H. L Cupples, and T. H. Tremearne, J. Am. Chem. Soc.,* **50,** 1275 (1928), *and E. P. Bartlett, H. C. Hetherington, H. M. Kvalnes, and T. H. Tremearne, J. Am. Chem. Soc.,* **52,** 1363 (1930).

temperature, he would need a graph of C vs. molal volume with temperature as parameter in order to read C directly. On the other hand, it is always possible to use the pT plot for this or other cases, by using a trial method of solution, as the following example shows:

Illustration 1.—What pressure in atmospheres would be developed by storing 10 lb.-moles of nitrogen in a volume of 15 cu. ft. at 200°C.?

$$p = \frac{CNRT}{V}$$

For a first trial, assume $C = 1$. Then

$$p = \frac{10 \times 1.315 \times 473}{15} = 415 \text{ atm.}$$

From Fig. V.1, $\qquad C = 1.245$

A second trial using $C = 1.40$ gives $p = 580$; at this pressure, $C = 1.37$. From this it is evident that the correct pressure is between 415 and 580 atm. and much nearer the latter.

Assuming $C = 1.35$, $p = 560$, and, from the figure, $C = 1.345$. This is close enough agreement, and hence the desired pressure is 560 atm.

This problem can also be solved graphically without a trial process in the following manner:

$$\frac{pV}{NRT} = C = \frac{p \times 15}{10 \times 1.315 \times 473} = 0.00242p$$

This equation represents a straight line on Fig. V.1 passing through the origin ($p = 0$, $C = 0$) and the point $p = 800$, $C = 1.935$. Where this line crosses the $t = 200°C$. isotherm, we can read the pressure directly as 560 atm. For this particular figure the origin is not included but another point, for example, $C = 0.800$, $p = 330$, will do just as well.

Another compressibility factor is frequently used; it is defined by the equation[1]

$$A = \frac{pv}{p_s v_s} \tag{V.15}$$

where $p_s v_s$ is the pv product at standard conditions, *viz.*, the ice point and a pressure of 1 atm. If the pressure is expressed in atmospheres and the volume in terms of the standard-condition volume as the unit, then we can write

$$A = pv$$

The relation between the two compressibility factors is given by

$$C = AC_s \frac{T_0}{T} \tag{V.16}$$

T_0 is the ice-point temperature and C_s is the compressibility factor [defined by Eq. (V.14)] at standard conditions. C_s differs very little from unity, and for most engineering calculations we can write Eq. (V.16) in the form

$$C = A \frac{T_0}{T} \tag{V.17}$$

For the highest accuracy one cannot assume that the ideal-gas law holds at 1 atm. but only at the limit as p approaches 0. The density of various gases has been measured at pressures less than 1 atm. and the results extrapolated to $p = 0$, by means of the equation,

$$pv = a + bp + cp^2 \tag{V.18}$$

In this way, one obtains the value of $p_0 v_0$, the pv product at the limit where $p = 0$. The ratio $p_0 v_0 / p_s v_s$ (frequently represented as $1 + \lambda$) for a number of gases at $0°C$. is given in Table V.1. For most gases the difference between $p_0 v_0$ and the value of the pv product at 1 atm. is negligible, but in some cases the difference may be as great as 4 per cent.

---

[1] This ratio is sometimes called an "Amagat unit" after the French physicist who was a pioneer in the study of the compressibility of gases.

Gas	Limiting Value of A at 0°C. as $p \to 0$
A	1 0009
H_2	0.9993
He	0.9995
N_2	1.0004
O_2	1 0009
HCl	1.0074
HI	1.015
SO_2	1.024
NO	1.0011
NH_3	1.015
CO	1.0005
CO_2	1.0070
CH_4	1.0024
C_2H_4	1.0078
$(CH_3)_2O$	1.0254
n-Butane	1.042*

* JESSEN, F. W., and J. H. LIGHTFOOT, *Ind. Eng. Chem.*, **28**, 870 (1936).

Reduced Coordinates.—The compressibility-factor graphs (Fig. V.1) will be different for every gas, but they will all show the same general trends. There is a physicochemical law which states that all gases behave alike when in corresponding states, *i.e.*, when any two of the variables, pressure, volume, and temperature, bear a given ratio to the critical values. This so-called "law of corresponding states" is not an exact one by any means, but it is a very useful approximation. Thus, if we define a reduced pressure, reduced temperature, and reduced volume as follows:

$$p_R = \frac{p}{p_c} \qquad \text{(V.19)}$$

$$T_R = \frac{T}{T_c} \qquad \text{(V.20)}$$

$$v_R = \frac{v}{v_c} \qquad \text{(V.21)}$$

where the subscript c refers to the critical state, the law states that any two gases when considered at the same p_R and T_R will have the same value of v_R and also the same value of the compressibility factor and the thermodynamic properties.

Newton[1] has shown that better agreement is obtained in representing the property f/p as a function of p_R and T_R for hydrogen, helium, and neon, if special reduced conditions are used for these gases defined as follows:

[1] NEWTON, R. H., *Ind. Eng. Chem.*, **27**, 302 (1935).

$$T_R = \frac{T}{T_c + 8} \tag{V.22}$$

$$p_R = \frac{p}{p_c + 8} \tag{V.23}$$

We shall also use these modified definitions in representing the compressibility factors of the same gases.

To show more specifically what the law of corresponding states means, consider the following example: Hydrogen, which has a critical temperature of 33.2°K. and critical pressure of 12.8 atm., will have at −190.7°C. ($T_R = 2.0$) and at 2.08 atm. pressure ($p_R = 0.10$) approximately the same values of thermodynamic properties as carbon dioxide at 335.3°C. ($T_R = 2.0$) and at 7.30 atm. pressure ($p_R = 0.10$).

The use of reduced coordinates allows us to introduce a very great simplification into the question of representing the behavior of actual gases, for if we plot C in terms of reduced pressures and temperatures, we can use one graph for all gases. Figure V.2 shows such a graph for reduced pressures up to 10, and Fig. V.3 extends the range of pressures to higher values. These graphs are based on a comprehensive survey of compressibility data in the literature. Data on about 20 different gases are involved.

The deviations between the compressibility factors based on experimental data and those read from these figures were extensively investigated. For 263 individual cases covering all ranges on the figures and 18 different gases, the average deviation was a little under 2 per cent. The worst case was ammonia, for which deviations as high as 15 per cent were found; the average for this gas was 7 per cent. From these figures it appears safe to conclude that these generalized charts will give sufficient accuracy for most engineering calculations. Graphs similar to Figs. V.2 and V.3 were first developed by Cope, Lewis, and Weber[1] and Brown, Souders, and Smith[2] for hydrocarbons and later extended by Dodge[3] to include other substances.

Another correlation sometimes used is a graph of p_R vs. T_R at constant values of v_R. This has the advantage that the reduced isometrics (reduced constant-volume lines) are nearly linear and hence interpolation is somewhat easier, but it suffers from the great disadvantage that critical-volume data are very meager and not very accurate.

These graphs show at a glance the way in which any gas deviates from the ideal state. At low pressures all gases approach ideality

[1] Cope, J. Q., W. K. Lewis, and H. C. Weber, *Ind. Eng. Chem.*, **23**, 887–892, (1931).

[2] Brown, G. G., M. Souders, and R. L. Smith, *Ind. Eng. Chem.*, **24**, 513–515 (1932).

[3] Dodge, B. F., *Ind. Eng. Chem.*, **24**, 1353–1363 (1932).
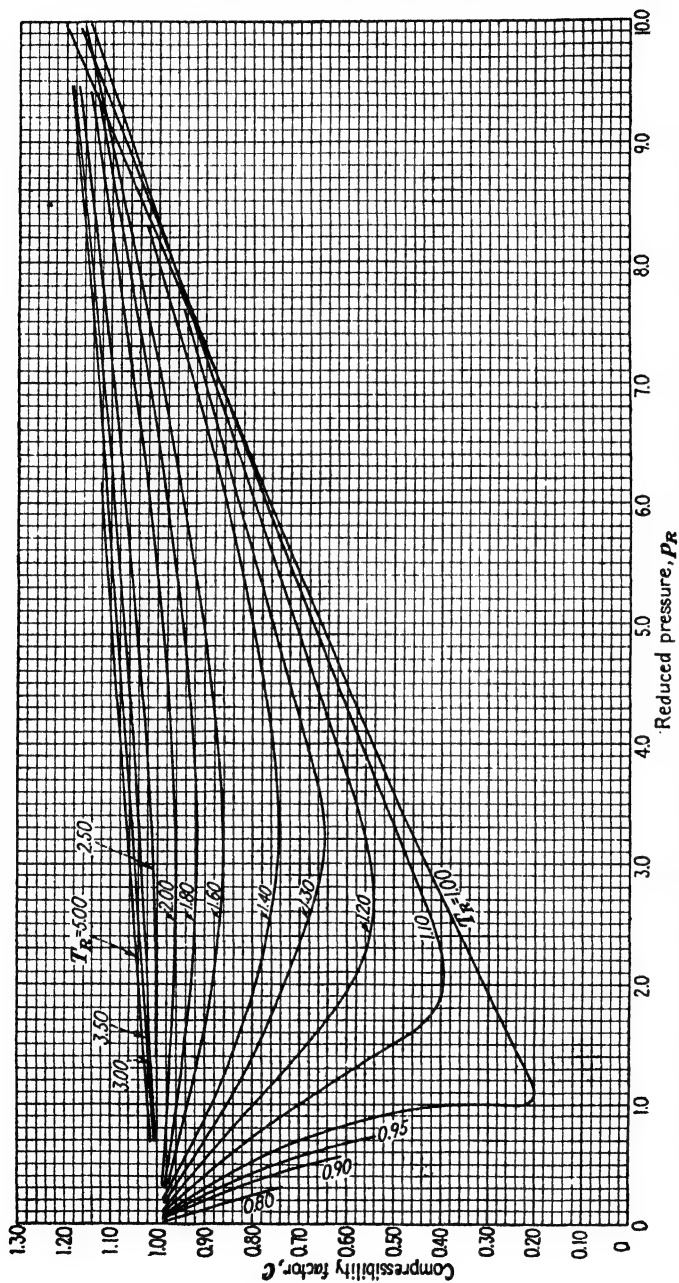
Fɪɢ. V.2.—Compressibility factor versus reduced pressure for a series of reduced temperatures. (Low-pressure range.)

$(C = 1.00)$. At temperatures below the critical temperature $(T_R < 1)$ or at temperatures not far above the critical and at moderate pressures, all gases occupy volumes less than that of the ideal gas (or have greater density), and as the pressure is increased the deviation becomes greater in the same direction until a minimum point is reached beyond which
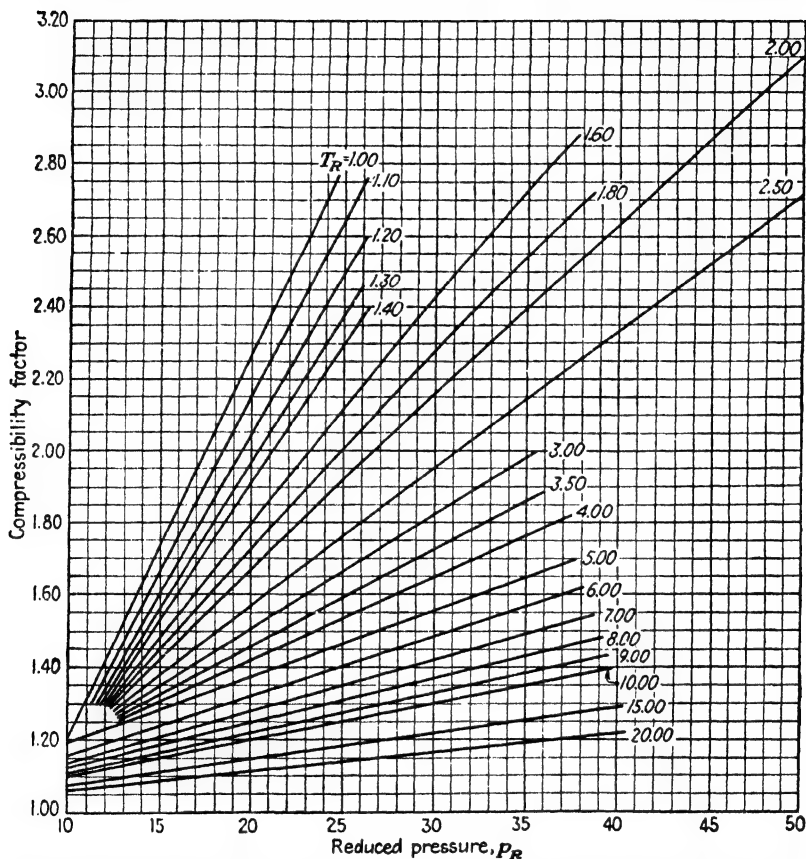
FIG. V.3.—Compressibility factor versus reduced pressure for a series of reduced temperatures. (High-pressure range.)

the deviation becomes less (compressibility factor greater). Finally, at a certain reduced pressure, the volume becomes equal to that of the ideal gas; and then, as pressure increases still further, the deviations are all in the other direction, or the volume of the actual gas is greater than that of the ideal gas. When the reduced temperature is greater than 2.5 (approximately), the deviations *for all pressures* are in the direction of a volume greater than the ideal. The two regions, *i.e.*, the one in which

the deviations are negative (actual volume less than ideal) and the other in which they are positive, are roughly characterized by the fact that in the first region the force of attraction between the molecules is the dominating factor and in the other the controlling factor is the actual volume of the molecules themselves. The temperature at which the transition occurs from a compressibility factor less than 1.00 to one greater than 1.00 at low pressure ($p = 0$ at the limit) is known as the "Boyle point." It is a different temperature for all gases, but when expressed in reduced units it is approximately 2.5 for all gases. The definition of the Boyle point is given by the equation

$$\left[\frac{\partial(pv)}{\partial p} \right]_T = 0 \text{ as } p \to 0 \qquad (V.24)$$

Since $pv = CRT$, $\dfrac{\partial C}{\partial p} = \dfrac{1}{RT} \dfrac{\partial(pv)}{\partial p}$

and so $\partial C/\partial p = 0$ also at this point. The Boyle point has no practical value other than being a convenient reference point in discussing deviations from the ideal-gas law.

At temperatures above the Boyle point, the isotherms at first increase in slope as the temperature increases and then decrease. At a reduced pressure of 10, all gases deviate approximately the same amount, regardless of the temperature. This is more strikingly exhibited on the C-p charts for a given gas. For example, for CO all the isotherms from -70 to 200°C. cross very close to one point, *viz.*, $C = 1.217$ and $p = 375$ atm.[1]

The general statement sometimes made that all gases approach the ideal state as the temperature is increased at constant pressure is seen not to be true. It is true at temperatures below the Boyle point and also above this point at very high pressures, but at reduced pressures below 10 and at temperatures above the Boyle point there is a region where C is greater than 1.0 and increases as the temperature increases.

The maximum deviation from ideality, as far as these particular figures are concerned, occurs at the critical point where the ideal volume is approximately 3.7 times the actual volume observed. This figure is not independent of the nature of the gas, being as low as 3.05 for helium and as high as 4.78 for hydrogen cyanide. Below the critical isotherm the lines end abruptly at the reduced pressure corresponding to the vapor pressure beyond which the gas can no longer exist as a stable state. It is of interest to note that the deviations from the ideal state are relatively greatest of all in this region.

[1] BARTLETT, E. P., H. C. HETHERINGTON, H. M. KVALNES, and T. H. TREMEARNE, *J. Am. Chem. Soc.*, **52**, 1374 (1930).

The graphs of Figs. V.2 and V.3 may be used for the approximate estimation of the volume of any gas when supplemented by a table of the critical constants. Such a tabulation along with data on the van der Waals constants is given in the Appendix.

Illustration 2.—Estimate the volume in cubic feet of 1 lb.-mole of ethylene at 60°C. and 200 atm., and compare with the ideal volume.

From Eqs. (V.19) and (V.20) and data in Table IV, of the Appendix,

$$T_R = \frac{273.2 + 60}{282.8} = 1.177$$

$$p_R = \frac{200}{50.9} = 3.93$$

By interpolation in Fig. V.2,

$$C = 0.605$$

$$v = \frac{CRT}{p}$$

$$= \frac{0.605 \times 1.3145 \times 333}{200}$$

$$= 1.324 \text{ cu. ft.}$$

$$\text{Ideal volume} = \frac{1.324}{0.605} = 2.19 \text{ cu. ft.}$$

The actual compressibility data give $v = 1.330$.

Illustration 3.—What pressure would be developed if 100 cu. ft. of nitrogen measured at standard conditions were compressed into a volume of 0.250 cu. ft., the temperature being 100°F.?

From Eq. (V.14),

$$p_2 = p_1 \frac{C_2 v_1 T_2}{C_1 v_2 T_1} \qquad \text{(at constant mass)}$$

$$= \frac{(460 + 100)100 C_2}{0.250 \times 492} \qquad (C_1 \text{ assumed to be } 1.00)$$

$$= 455 C_2$$

Since $p_c = 33.5$,

$$p_2 = 33.5 p_{R_2} = 455 C_2$$

or

$$C_2 = 0.0736 p_{R_2}$$

This is a straight line on the C vs. p_R graph passing through the origin. The intersection of this line with the reduced isotherm $T_R = \frac{560}{126 \times 1.8} = 2.47$ gives the value of p_R. Using Fig. V.3, we get

$$p_R = 23.7$$

$$p = 23.7 \times 33.5 = 795 \text{ atm.}$$

These methods of calculation based on the reduced compressibility-factor chart are convenient but not highly accurate. For more accurate representation of the pvT behavior, one should prepare such charts for each individual gas with which he is concerned or use other methods to be explained presently.

Estimation of Critical Temperature.—Because of the importance of the critical state to the correlation of compressibility data and the difficulty of measuring the critical temperature it is important to develop

methods for its calculation from other properties more readily measured. One of the methods for doing this is that proposed by Watson[1] in which the critical temperature is calculated from the empirical equation

$$T_c = \frac{T_B + \Delta}{0.283 \ (M/\rho_B)^{0.18}} \tag{V.25}$$

M is the molecular weight and ρ_B is the density of the liquid at normal boiling point g/cc. Δ is a correction factor that equals $T_e - T_B$ where T_e is a temperature on the absolute scale at which the substance is in equilib-
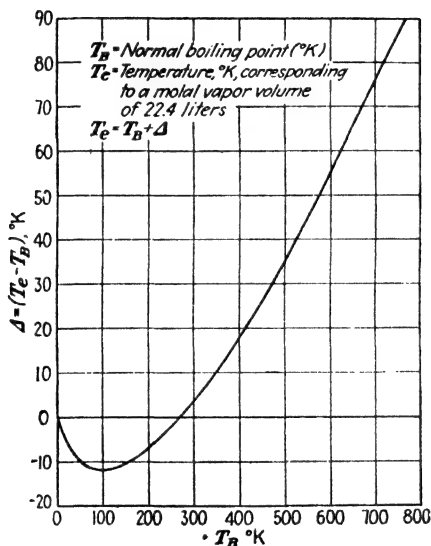
FIG. V.4.—Chart for the estimation of critical temperature.

rium with saturated vapor whose concentration is 1 g.-mole per 22.4 liters. The correction factor is estimated from the normal boiling point T_B by means of Fig. V.4 taken from Watson. This method was tested by Watson on a wide variety of substances and found to be accurate to about 2 per cent for nonpolar or slightly polar substances. For polar ones like water, acetic acid, and ammonia the method is not recommended.

The critical pressure, which is simply the vapor pressure at the critical temperature, may be estimated from vapor-pressure measurements by some of the methods discussed in Chap. VI.

Meissner and Redding[2] give the following empirical equations for prediction of critical temperature, volume, and pressure for either polar or nonpolar liquids:

[1] WATSON, K. M., *Ind. Eng. Chem.*, **23**, 360 (1931).
[2] MEISSNER, H. P.. and E. M. REDDING, *Ind. Eng. Chem.*, **34**, 521 (1942).

For compounds boiling below 235°K. or for all elements,

$$T_c = 1.70T_B - 2$$

where T_c = critical temperature, °K.

T_B = normal boiling point, °K.

For compounds boiling above 235°K.,

1. Compounds containing halogens or sulphur:

$$T_c = 1.41T_B + 66 - 11F$$

where F = number of fluorine atoms.

2. Aromatics and naphthenes (halogen- and sulphur-free):

$$T_c = 1.41T_B + 66 - r(0.383T_B - 93)$$

where r = ratio of noncyclic carbon atoms to the total.

3. All compounds (halogen- and sulphur-free) other than aromatics and naphthenes:

$$T_c = 1.027T_B + 159$$

For all substances:

$$v_c = (0.377P + 11.0)^{1.25}$$

where P = parachor of Sugden.

v_c = critical volume, cc. per g.-mole.

The parachor is computed from Sugden's basic equation

$$P = \frac{M(\sigma)^{\frac{1}{4}}}{\rho_L - \rho_V} \qquad \sigma = \text{surface tension}$$

ρ_L and ρ_V are liquid and vapor densities, respectively, in grams per cubic centimeter at room temperature. The parachor can also be computed from the structure of an organic compound using the following equivalents, which are additive:

TABLE V.2.—ATOMIC AND STRUCTURAL PARACHORS

Element	Parachor	Structural feature	Parachor
C	4.8		
H	17.1	Double bond	23.2
N	12.5	Triple bond	46.6
P	37.7	3-membered ring	16.7
O	20.0	4-membered ring	11.6
S	48.2	5-membered ring	8.5
F	25.7	6-membered ring	6.1
Cl	54.3	O_2 in esters	60.0
Br	68.0		
I	91.0		

The critical pressure is calculated from

$$p_c \ (\text{atm.}) = \frac{20.8T_c}{v_c - 8}$$

where T_c is in degrees Kelvin.

Calculated values for 42 substances are compared with the experimental values. In the case of T_c, the maximum deviation is ± 5 per cent. Excellent agreement is obtained for v_c with the exception of two cases, one of which is water, which is generally to be regarded as an anomalous substance as far as any general relationships are concerned. The calculated critical pressure is less accurate; but, except for 5 substances, the maximum error was 11 per cent.

Volume-delivered Chart.—One of the commonest types of problem encountered in dealing with gases under pressure is the calculation of the volume delivered from (or supplied to) a storage vessel of given size. If many such calculations are to be made for a given gas, it is desirable to construct a direct-reading chart to be used for this purpose. From Eq. (V.14),

$$\frac{v_2}{v_1} = \frac{C_2 T_2 p_1}{C_1 T_1 p_2} \tag{V.26}$$

If v_1 is taken as 1 cu. ft. and some standard conditions are selected for p_2 and T_2, the low-pressure volume v_2 is determined by the two variables p_1 and T_1. A convenient chart is made by plotting v_2 as a function of p_1 along a series of isotherms. Such a chart for oxygen over a limited range is given in Fig. V.5. Directly from the chart, one finds that, at 2,000 lb. gauge pressure and 95°F., the volume at 1 atm. and 70°F. is 137 cu. ft. from a 1 cu. ft. container. For any other size of container the volume delivered will be directly proportional to the size.[1]

EQUATIONS OF STATE

General Form and Derivation.—In general, an equation of state is an equation of the form,

$$\phi(p,V,T,m) = 0 \tag{V.27}$$

It is customary to deal with unit molal mass, and hence the usual form is

$$\phi(p,v,T) = 0 \tag{V.28}$$

For practical purposes, the most useful equation of state is one that gives the volume explicitly, as

$$v = \phi(p,T) \tag{V.29}$$

---

[1] For similar charts for several gases along with other useful information on the properties of gases see Relations between the Temperatures, Pressures, and Densities of Gases, *Bur. Standards Circ.* 279 (1926).

since p and T are the most generally used independent variables.   Most equations of state, however, have been derived on the basis of certain kinetic considerations, and this commonly leads to an equation which
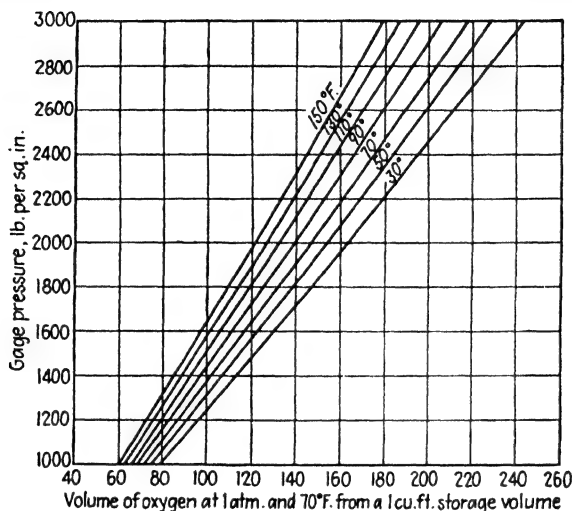
Fig. V.5.—Volume-delivered chart for oxygen.   (Data from International Critical Tables.)

gives the pressure explicitly.   Other equations may be purely empirical, for example, equations of the form

$$p = \frac{RT}{v} + \frac{A}{v^2} + \frac{B}{v^3} + \frac{C}{v^4} + \cdots \qquad (V.30)$$

and $$pv = a + bp + cp^2 + dp^3 + \cdots \qquad (V.31)$$

where A, B, a, b, etc., are functions of temperature also represented in purely empirical form by such an equation as

$$A = a_1 + \frac{a_2}{T} + \frac{a_3}{T^2} + \frac{a_4}{T^4} + \cdots$$

From the standpoint of practical application, all equations of state must be regarded as essentially empirical.   Even though they may have been derived by a sound application of kinetic theory, the constants have to be determined from actual experimental data.   Furthermore, no equation of state can be relied on to represent accurately the compressibility data much beyond the range of pressure and temperature for which the constants were determined.   In other words, they are empirical equations useful for interpolation, and they cannot be safely extrapolated. The derivation of the general form of the equation from kinetic theory probably has the advantage that it gives an equation which will represent

a large amount of data with a minimum number of constants—less than might be needed for an equation obtained on a wholly empirical basis.

Some equations of state have a thermodynamic rather than a kinetic basis for their derivation. For example, one may start with the fundamental equation for the Joule-Thomson effect, *viz.*,

$$T\left(\frac{\partial v}{\partial T}\right)_p - v = \mu C_p \qquad \text{(III.97)}$$

where

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H$$

Assuming μ and C_p to depend in some definite way on p and T, the differential equation could be integrated. Thus we might assume C_p a constant and μ to be independent of the pressure but related to temperature by the equation

$$\mu = \frac{a}{T^n}$$

where a and n are constants. Substituting this expression in Eq. (III.97) and rearranging a little,

$$\frac{T\,dv - v\,dT}{T^2} = \frac{aC_p}{T^{n+2}}\,dT$$

or

$$d\,\frac{v}{T} = aC_p\,\frac{dT}{T^{n+2}}$$

Integrating at constant pressure,

$$\frac{v}{T} = -\frac{aC_p}{(n+1)T^{n+1}} + \phi(p) \qquad \text{(V.32)}$$

If we assume that the state of an ideal gas is approached as T approaches infinity along an isobar,

$$\frac{v}{T} = \frac{R}{p} \qquad \text{(at large values of } T\text{)}$$

then

$$\phi(p) = \frac{R}{p}$$

and Eq. (V.32) becomes

$$v = \frac{RT}{p} - \frac{aC_p}{n+1}\frac{1}{T^n} \qquad \text{(V.33)}$$

This equation is sometimes known as the Callendar equation of state since it was used by Callendar in his work on the properties of steam.

Limiting Conditions.—There are certain limiting conditions and general trends that must be satisfied by any equation of state. Some of the more important are as follows:

1. $pv = RT$ as $p \to 0$ at any temperature. In other words, the equation of state should reduce to the ideal-gas equation at low pressures. On the other hand, it should be noted that the quantity α, which equals

$(RT/p) - v$, does not necessarily approach zero as $p \rightarrow 0$ at constant temperature. Figure V.6 shows the behavior of α vs. p isotherms for carbon monoxide and methane.
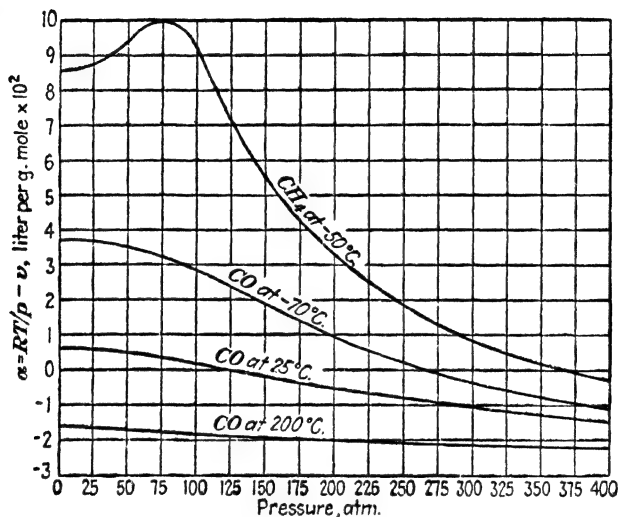
FIG. V.6.—Isotherms of α vs. p.

The fact that $pv \rightarrow RT$ but that $(RT/p) - v$ does not approach zero may seem paradoxical at first sight, but it may perhaps be made a little clearer by the following simple demonstration:

By definition,
$$\frac{RT}{p} - v = \alpha$$
where α is a finite quantity.

Multiplying both sides by p,
$$RT - pv = \alpha p$$
when $p = 0$, $\alpha p = 0$, and $pv = RT$ even though $\alpha \neq 0$.

It may also be readily demonstrated from the following equation, which has been shown[1] to represent accurately the isotherms of permanent gases up to 100 atm.:

$$pv = RT + ap + bp^2 + cp^4 \tag{V.34}$$

or
$$v = \frac{RT}{p} + a + bp + cp^3 \tag{V.35}$$

When $p = 0$, $pv = RT$ by Eq. (V.34)

and
$$\frac{RT}{p} - v = -a \qquad \text{by Eq. (V.35)}$$

[1] HOLBORN, L., and J. OTTO, *Z. Physik*, **33**, 1 (1925).

2. The limiting value of v/T along an isobar is a quantity that comes into several problems, as will be seen later.   From the ideal-gas equation, it might be expected that

$$\lim_{\frac{1}{T} \to 0} \frac{v}{T} = \frac{R}{p} \qquad (V.36)$$

Most of the equations of state explicit in v, as may be seen from the equations given later in this chapter, reduce to Eq. (V.36) at the limit where $1/T \to 0$, but some studies of experimental data do not bear this out.   This point cannot be regarded as definitely settled yet; for the time being, we shall assume that Eq. (V.36) represents the limiting behavior along an isobar.

3. The slope of the pv vs. p curves (or the curves of compressibility factor vs. pressure) at constant temperature, which equals zero at all temperatures for an ideal gas, may in the case of actual gases be equal to, greater than, or less than zero as p approaches zero, depending on the temperature (see Fig. V.3, for example).   Expressing this mathematically,

$$\left[\frac{\partial(pv)}{\partial p} \right]_T \underset{<}{\overset{>}{=}} 0 \qquad (\text{as } p \to 0) \qquad (V.37)$$

When the derivative is set equal to zero, we have the criterion for the Boyle point.   It is greater than 0 at all temperatures higher than this point, and vice versa.

4. The critical isotherm, *i.e.*, the curve relating pressure and volume at the critical temperature, must show a point of inflection, or, mathematically,

$$\left(\frac{\partial p}{\partial v} \right)_{T_c} = 0 \qquad (V.38)$$

and

$$\left(\frac{\partial^2 p}{\partial v^2} \right)_{T_c} = 0 \qquad (V.39)$$

5. The pT curves (isometrics) are substantially linear except at very high densities, or

$$\left(\frac{\partial^2 p}{\partial T^2} \right)_v = 0 \qquad (V.40)$$

approximately for most conditions and exactly as $T \to \infty$.

At high density,

$$\left(\frac{\partial^2 p}{\partial T^2} \right)_v < 0 \qquad (V.41)$$

or the isometrics are convex upward from the T axis.

Van der Waals' Equation.—One of the earliest attempts to represent the behavior of actual gases by an equation was that of van der Waals about 1873.   He proposed the following equation known by his name:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{V.42}$$

or

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \tag{V.43}$$

This differs from the ideal-gas equation by the addition of the term a/v^2 to the pressure and the subtraction of a term b from the volume. a/v^2 is the correction of the pressure due to the forces of attraction between the molecules; it is sometimes called the " cohesive pressure" or the "internal pressure."   In other words, the actual pressure p exerted by the gas on the walls of the vessel is less than the ideal pressure p_i by an amount a/v^2 or $p = p_i - (a/v^2)$.   The constant b is to be regarded as the correction to the total volume due to the actual volume occupied by the molecules themselves. a and b are constants characteristic of the particular gas, whereas R is still the universal gas constant.   The temperature is, of course, on the absolute scale; and v is either the specific volume or the molal volume, as one chooses.

Let us now see how this equation agrees with the five criteria mentioned above.   As to criterion 1, it is readily apparent that, as $v \to \infty$, the equation approaches $pv = RT$.

The equation can be put in the form

$$v = \frac{RT}{p} + b - \frac{a}{pv} - \frac{b}{pv^2} + \frac{ab}{pv^2} \tag{V.44}$$

or

$$\frac{RT}{p} - v = \alpha = \frac{a}{pv} + \frac{b}{pv^2} - \frac{ab}{pv^2} - b$$

As $p \to 0$,

$$\alpha = \frac{a}{pv} - b = \frac{a}{RT} - b \tag{V.45}$$

or α approaches a finite value as $p \to 0$ along an isotherm.

Dividing Eq. (V.44) by T, one gets

$$\frac{v}{T} = \frac{R}{p} + \frac{b}{T} - \frac{a}{pvT} - \frac{b}{pv^2T} + \frac{ab}{pv^2T}$$

As $1/T \to 0$ at constant p,

$$\frac{v}{T} = \frac{R}{p}$$

and criterion 2 is satisfied.

By differentiating the pv product with respect to p, one gets

$$\left[\frac{\partial(pv)}{\partial p}\right]_T = v + p\left(\frac{\partial v}{\partial p}\right)_T$$

Evaluating the right-hand side from the equation of state and taking the limit as $p \to 0$ or $v \to \infty$,

$$\left[\frac{\partial(pv)}{\partial p} \right]_T = b - \frac{a}{RT}$$

Placing this equal to zero, one gets

$$T = \frac{a}{bR} \qquad (V.46)$$

where T is the Boyle point. At temperatures greater than this value of T, the slope $\partial(pv)/\partial p$ at $p = 0$ is readily seen to be greater than 0 and
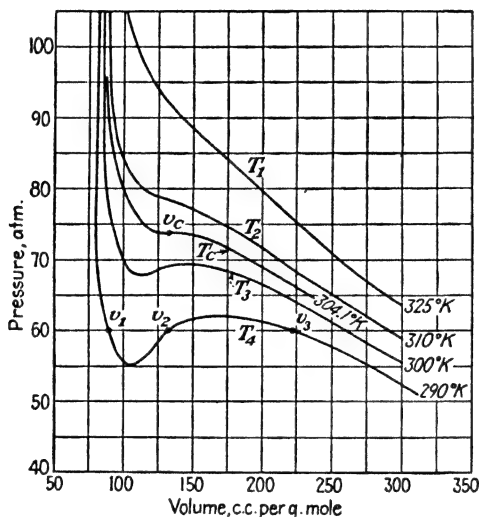
Fig. V.7.—Van der Waals' isotherms for carbon dioxide near the critical point.

at all values of T less than T_{Boyle} it is less than 0. Therefore, the van der Waals' equation meets condition 3.

The equation is a cubic in v, as a simple rearrangement will show. In other words, there are three roots, or three values of v for a given p and T. On the other hand, these roots may not be all real; as a matter of fact, it is easy to show that, above a certain value of T, there are only one real root and two imaginary ones. Below this value there are three real roots, and at this value of T there are three equal roots, *i.e.*, a point of inflection on the pv curve. The state of affairs predicted by the van der Waals' equation is represented graphically in Fig. V.7. Along the isotherms T_1 and T_2 there is only one real root, or only one value of v for a given p. As the temperature is lowered, there appears a temperature

T_c for which there is a point of inflection on the p vs. v curve—*i.e.*, a unique or critical point.   At lower temperatures, such as T_4, there are some pressures for which there are three real and unequal volumes, for example, v_1, v_2, and v_3.   This behavior predicted for temperatures below the critical is, of course, not in accord with the observed facts, at least for equilibrium states.   Actually, instead of a continuous change as indicated by the equation, there is an abrupt change at some point such as v_1, due to the appearance of a second phase.   From that point on, the pressure remains constant as the volume decreases until the point v_3 is reached and the first phase disappears; after that the pressure drops as the volume is increased.   We see, therefore, that the van der Waals' equation predicts the critical phenomena and is in accord with the general trend of the pv curves above the critical temperature.

From Eqs. (V.38) and (V.39), we have

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 = \frac{-RT}{(v-b)^2} + \frac{2a}{v^3} \tag{V.47}$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0 = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} \tag{V.48}$$

From these two equations and the van der Waals' equation, one gets

$$v_c = 3b \tag{V.49}$$

$$T_c = \frac{8a}{27Rb} \tag{V.50}$$

$$p_c = \frac{a}{27b^2} \tag{V.51}$$

These equations enable one to compute the coordinates of the critical point from the constants a and b of the equation.   Practically, one reverses this procedure and calculates a and b from the experimentally determined values of p_c and T_c, using the following equations obtained from Eqs. (V.50) and (V.51):

$$a = \frac{27}{64}\frac{R^2T_c^2}{p_c} \tag{V.52}$$

$$b = \frac{RT_c}{8p_c} \tag{V.53}$$

Values of a and b calculated from these equations are given in Table IV in the Appendix.   Of course, one can also treat a and b as empirical constants and determine their best values for a given set of data.   This will, in general, give an equation that represents these particular data better than one with the constants determined by Eqs. (V.52) and (V.53). It should be recognized, however, that the van der Waals' equation is only an approximation at best; its chief usefulness lies in its application to

preliminary calculations where few data are available and where accuracy is sacrificed to convenience.

Applying criterion 5, we find that

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - b}$$

and

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0$$

and therefore the equation demands linear isometrics.

We have seen that the van der Waals' equation represents certain general trends correctly, but it remains to show how nearly it agrees quantitatively with the behavior of actual gases. From Eqs. (V.49), (V.50), and (V.51), we find that

$$\frac{p_c v_c}{RT_c} = \frac{3}{8} \qquad (V.54)$$

or the compressibility factor at the critical point has the same value for all gases. Reference to Table IV in the Appendix shows that this factor varies appreciably from this value and is by no means the same for all gases. Since the value would be 1.00 for an ideal gas, it is clear that this equation is a very much closer approximation to the truth than the ideal-gas equation.

Substituting for a and b in Eq. (V.46) the values given by Eqs. (V.52) and (V.53), we have, for the Boyle point,

$$T_{\text{Boyle}} = 3.375 T_c \qquad (V.55)$$

Actually, T_{Boyle} does not bear the same ratio to the critical temperature for all gases but varies considerably with an average value of about 2.5 T_c.

The calculation of pressure by means of the van der Waals' equation, given volume and temperature, or of temperature, given pressure and volume, is relatively simple and straightforward and needs little comment. It should be noted that the v in the equation is a specific or molal volume. Thus, if it were desired to calculate the pressure developed in a vessel of V cu. ft. volume when m lb. of a gas is put into it at a temperature T, it is necessary only to calculate the specific volume V/m or the molal volume MV/m and substitute directly in the equation. If the initial volume at the low pressure rather than the weight were given, the weight can be calculated with sufficient accuracy from the ideal-gas law if the pressure is not far from atmospheric. If greater refinement is desired, the van der Waals' equation can be applied to both states of the gas; but this refinement is scarcely warranted in view of the approximate nature of the equation.

The calculation of the volume from the van der Waals' equation, given the pressure and the temperature, is most simply accomplished by a trial process.

Illustration 4.—What would be the volume occupied by 10 lb. of CO_2 at 50 atm. pressure and 100°C.?

From Table IV in the Appendix the constants a and b are 925 and 0.686, respectively. In the absence of any idea whatever of the magnitude of the volume, the first trial might conveniently be made by using the ideal-gas volume, which is easily obtained as follows:

$$v = \frac{RT}{p} = \frac{1.3145 \times 373.2}{50} = 9.80 \text{ cu. ft./lb.-mole}$$

Substitution of this value of v in Eq. (V.43) gives

$$p = 44.2$$

a value that is too low. From this first trial, it is evident that the next trial volume must be smaller. The following shows the result of several trials:

$$v = 9.00 \qquad p = 47.59 \text{ atm.}$$
$$= 8.00 \qquad = 52.62 \text{ atm.}$$
$$= 8.40 \qquad = 50.48 \text{ atm.}$$
$$= 8.45 \qquad = 50.23 \text{ atm.}$$
$$= 8.49 \qquad = 50.03 \text{ atm.}$$
$$= 8.495 \qquad = 50.00 \text{ atm.}$$

The final result can be obtained with sufficient accuracy by linear interpolation between close trials on either side.

$$\text{Volume of 10 lb.} = \frac{10}{44} \times 8.495 = 1.930 \text{ cu. ft.}$$

The degree of accuracy obtained with the use of the van der Waals' equation when the constants are derived from the critical pressure and temperature is shown in Table V.3 for a few cases intentionally chosen to give a rather severe test.

TABLE V.3.—APPLICABILITY OF THE VAN DER WAALS' EQUATION

Gas	T, °K.	p, atm.	T_R	p_R	Volume, cu. ft./lb.-mole		
					Observed	van der Waals	Ideal
CO_2	313.1	72.16	1.03	0.99	3.21	3.35	5.70
		100.0		1.387	1.11	1.43	4.12
N_2	273.1	200	2.165	5.96	1.860	1.775	.795
		1,000		29.8	0.741	0.863	0.359
H_2	273.1	200	8.22	15.6	2.036	2.082	1.795
		1,000		78.0	0.615	0.748	0.359
NH_3	323.1	20.06	0.795	0.180	17.25	19.10	21.15

In all cases except that of nitrogen at 200 atm., van der Waals' equation is a considerable improvement over the ideal-gas one, and the condition of the nitrogen happened to fall near the point (see Fig. V.1) where the equation of the ideal gas is exactly obeyed though the gas is actually far from the ideal state. There are, of course, a number of particular states for any given gas where the gas is by no means ideal but where the ideal-gas equation is exactly obeyed (locus of all points where $C = 1.000$). In all cases chosen, with one exception, the density was of the order of the critical density, and in the case of the ammonia one is dealing with a saturated vapor.

Before leaving the subject of the accuracy of the van der Waals' equation, it should be pointed out that the degree of agreement obtained depends on the quantity being calculated. From Table V.3 it is evident that van der Waals is much better for the calculation of the volume of N_2 at 0°C. and 1,000 atm. than the ideal-gas law; but if we take the observed volume and calculate the pressure at 0°C., it is 484 by the ideal-gas equation and 2,293 by van der Waals. Both are very seriously in error, and it is impossible to say that either equation gives a better result in this case.

Reduced Equations of State.—By substituting the values of a, b, and R given by Eqs. (V.52), (V.53), and (V.54) into the van der Waals' equation, the following equation results:

$$\left(p_R + \frac{3}{v_R^2}\right)(3v_R - 1) = 8T_R \qquad (V.56)$$

where p_R, v_R, and T_R are the reduced variables of state previously defined. This equation contains no arbitrary constants characteristic of individual gases; *i.e.*, it is a universal equation of state applying to all "van der Waals' gases." All gases may be said to be alike when considered at the same fractions of (or ratios to) the critical state values, or they are said to be in *corresponding states*. Thus the theory of corresponding states, which we made effective use of earlier in the chapter to present a compact picture of the behavior of real gases, rests largely on the applicability of the van der Waals' equation or other equations of state containing not more than three constants (in addition to the gas constant R). Since no one of these equations is accurate over the whole field of pvT changes, it is clear that the law of corresponding states, and deductions based on it, are only approximations. Nevertheless, it does introduce a great simplification, and the accuracy is ample for many engineering purposes.

Let us now apply the reduced equation of state (V.56) to make a few deductions about the behavior of gases. For example, consider the variation of the pv product with pressure at constant temperature (deviation from Boyle's law). Substitute $x = p_R v_R$ in Eq. (V.56), and obtain

$$\left(1 + \frac{3p_R}{x^2}\right)(3x - p_R) = 8T_R \qquad (V.57)$$

Differentiate Eq. (V.57) at constant temperature, and put $\partial x / \partial p_R = 0$. The resulting expression is

$$x(9 - x) = 6p_R \qquad (V.58)$$

This relation between $p_R v_R$ and p_R, plotted in Fig. V.8, gives the loci of all the points where curves of pv vs. p have a minimum value. Each point on the locus curve corresponds to a different temperature, the latter increasing as pv increases. When $p_R = 0$, $p_R v_R = 0$ and 9. When $p_R v_R = \frac{2}{3}$, $p_R = 3.375$, the maximum value of p_R. From Eq. (V.57),

$$
\begin{aligned}
T_R &= 1.90 \quad && \text{when} \quad && p_R v_R = \tfrac{2}{3} \quad && \text{and} \quad && p_R = 3.375 \\
&= 3.375 \quad && \text{when} \quad && p_R v_R = 9.0 \quad && \text{and} \quad && p_R = 0
\end{aligned}
$$

In terms of the behavior of actual gases, this means that the minima in the pv vs. p curves shift to the right as the temperature increases, until finally on the isotherm $T_R = 1.90$ a limit is reached; for all higher temperatures the minima shift to the left; at $T_R = 3.375$ (Boyle point) the minimum occurs at $p = 0$; for all higher temperatures there is no minimum. Applying this to actual gases at temperatures in the region of room temperature, ethylene ($T_R = 0.95$ at 25°C.) should exhibit a shift to the right in the minima on the pv vs. p isotherms, nitrogen ($T_R = 2.37$ at 25°C.) a shift to the left, and hydrogen ($T_R = 8.98$ at 25°C.) should show no minima. These deductions are in accord with the observed facts. Quantitative predictions, of course, cannot be relied on for accuracy, as already pointed out. In a similar way, we may deduce certain qualitative facts about the Joule-Thomson effect in gases, but the method is analogous to that already given for the Boyle point and will not be presented.

FIG. V.8.—Locus curve for minima on reduced pv vs. p curves.

Equations of Berthelot and Dieterici.—A very large number (over 100) of equations of state have been proposed, but only a very few have come into common use. It is our intention to discuss several different ones very briefly and then to concentrate attention on two equations that have been widely employed in the American literature.

Two of the early attempts to improve on the van der Waals' equation led to the following equations:

$$p = \frac{RT}{v - b} e^{-\frac{a}{RT_v}} \quad \text{(Dieterici equation)} \quad \text{(V.59)}$$

$$p = \frac{RT}{v - b} - \frac{a}{Tv^2} \quad \text{(Berthelot equation)} \quad \text{(V.60)}$$

These are both two-constant equations like the van der Waals'; hence, the constants a and b may be related to the critical constants in the same way and the equations may also be put in a reduced form.   The
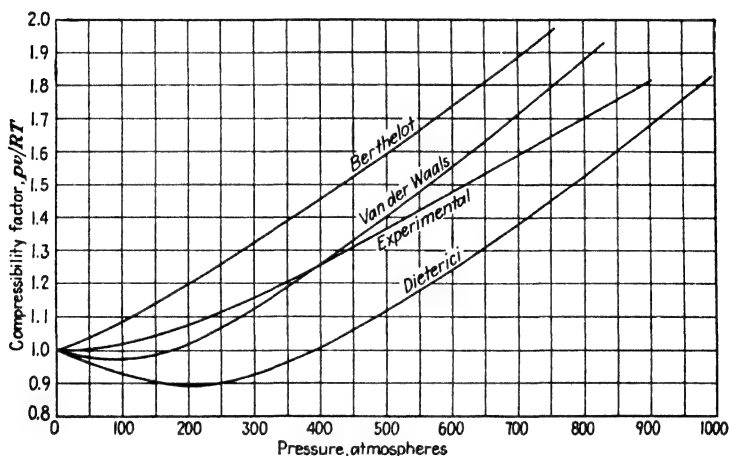
Fig. V.9.—Comparison of van der Waals', Berthelot, and Dieterici equations with observed data on nitrogen at 50°C.

equations for the constants of the Dieterici and Berthelot equations, respectively, are as follows:

$$a = \frac{4R^2T_c^2}{p_c e^2} \quad \text{(V.61)}$$

$$b = \frac{RT_c}{p_c e^2} \quad \text{(V.62)}$$

$$a = \frac{27}{64} \frac{R^2T_c^3}{p_c} \quad \text{(V.63)}$$

$$b = \frac{RT_c}{8p_c} \quad \text{(V.64)}$$

For the Berthelot equation, the following empirical equations are said to give better results in practice:

$$\frac{RT_c}{p_c v_c} = \frac{32}{9} \quad \text{(V.65)}$$

$$b = \frac{9}{128} \frac{RT_c}{p_c} \quad \text{(V.66)}$$

The equation for a remains the same as Eq. (V.63).

No generally valid statement can be made about the accuracy with which these two equations represent the pvT data of various gases as compared to van der Waals' equation. Each of the equations in turn is the best in a given case as one varies the gas or even the conditions with a given gas. In Figs. V.9 and V.10 there is shown a comparison of the three equations with observed data for two different gases. These particular gases were chosen because one is near its critical temperature and the other well above it. The constants for the Berthelot equation were calculated from Eqs. (V.63) and (V.64). For a more
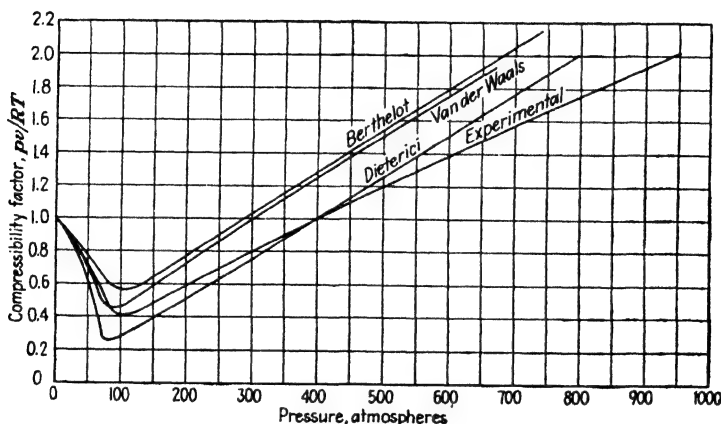
FIG. V.10.—Comparison of van der Waals', Berthelot, and Dieterici equations with observed data on ethylene at 40°C.

detailed comparison of these three equations, reference should be made to the Bureau of Standards Circular 279.

Wohl Equation.—This equation, which is

$$p = \frac{RT}{v - b} - \frac{a}{v(v - b)} + \frac{c}{v^3}$$

is of interest because it has three constants that can be evaluated from the critical constants. The equations for this purpose are

$$a = 6v_c^2 p_c$$
$$b = \tfrac{1}{4}v_c$$
$$c = 4v_c^3 p_c$$

The critical volume is seldom known accurately, and it can be eliminated through the relation

$$v_c = \frac{RT_c}{3.75p_c}$$

According to the studies made by Wohl,[1] the equation gives excellent results over wide ranges, and if this is correct it deserves more notice than it has received.

Some Explicit-volume Equations.—All the equations so far discussed have been of the explicit-pressure, linear isometric type. For some applications it is more convenient to have an equation that gives the volume explicitly. Two equations of this type that have been useful in engineering work are the Goodenough and Linde equations, respectively:

$$v = c + \frac{RT}{p} - \frac{m}{T^n}(1 + 3ap^i) \qquad (V.67)$$

where c, m, n, and a are empirical constants.

$$pv = AT - \frac{p(C + Ep)}{T^3} + p(D + Fp) \qquad (V.68)$$

where A, C, D, E, and F are empirical constants. (Note that A should be identical with the gas constant R.) The Goodenough equation in a somewhat modified form was used in the correlation of the thermodynamic properties of steam.[2] The Linde equation originally proposed by Linde for superheated steam was used to calculate the thermodynamic properties of some petroleum distillates.[3]

The Bureau of Standards[4] used the following equation in deriving the thermodynamic properties of superheated ammonia vapor:

$$v = \frac{AT}{p} - \frac{B}{T^3} - \frac{C + Dp}{T^{11}} - \frac{Ep^5}{T^{19}} - F + \phi(p) \qquad (V.69)$$

A, B, C, D, E, and F are empirical constants, and $\phi(p)$ is given by the equation

$$\phi(p) = a + bp + cp^2 + dp^3$$

This equation contains 10 empirical constants, and we have given it largely to illustrate the fact that accurate representation of the pvT behavior of gases, even over rather limited ranges, may require a complex equation with many adjustable constants. In spite of this complexity an equation of state is justified by the great convenience it offers in the process of calculating thermodynamic properties. In computing the new values for the thermodynamic properties of steam, Keyes and coworkers[5] found it necessary to develop an equation with 10 empirical

[1] WOHL, A., *Z. Physik. Chem.*, **87**, 1–39 (1914).

[2] DAVIS, H. N., *Mech. Eng.*, **47**, 107–108 (1925).

[3] BAHLKE, W. H., and W. B. KAY, *Ind. Eng. Chem.*, **24**, 291–301 (1932).

[4] Tables of Thermodynamic Properties of Ammonia, *Bur. Standards Circ.* 142 (1923).

[5] KEYES, F. G., L. B. SMITH, and H. T. GERRY, *Proc. Am. Acad. Arts Sci.*, **70**, 319–364 (1936).

constants, and even then the equation was not valid for saturated vapor volumes less than 10 cc. per g.

Keyes Equation.—An equation that reproduces a wide range of experimental data with very good accuracy considering the small number of constants it contains was proposed by Keyes[1] and is as follows:

$$p = \frac{RT}{v - \delta} - \frac{A}{(v - l)^2} \tag{V.70}$$

where

$$\delta = \beta e^{-\frac{\alpha}{v}} \tag{V.71}$$

α, β, A, and l are empirical constants. By inspection this is seen to be a modified form of the van der Waals' equation. Like the latter it calls for linear isometrics, but it has two more arbitrary constants and therefore would be expected to be capable of more accurate representation of the actual facts. Owing to the number of constants it contains it cannot be put in a reduced form. Another disadvantage under which it labors is that it is not convenient for the evaluation of certain thermodynamic properties because the integral $\int dv/(v - \beta e^{-\frac{\alpha}{v}})$ that occurs cannot be evaluated in terms of simple functions.

The determination of the constants of the Keyes equation is relatively simple, and in the process of determination one sees how well the equation fits the data, which is a great practical advantage. Furthermore, there is the added practical advantage that only a limited amount of data is required. A brief outline of the procedure will be given because it illustrates some important points. The pvT data must first be arranged in the form of isometrics, *i.e.*, a series of pressure and temperature values at constant volume. The experimental method devised by Keyes gives the data directly in this form, but data in the form of pv values along isotherms can be treated graphically to put them in the isometric form. The equation of an isometric is

$$p = \psi T - \phi \tag{V.72}$$

where

$$\psi = \frac{R}{v - \delta} \tag{V.73}$$

and

$$\phi = \frac{A}{(v - l)^2} \tag{V.74}$$

Thus ψ and ϕ are functions of volume only, and their values for each isometric are readily determined by the usual methods for the constants of a straight line. From Eq. (V.74) we get

$$v = l + \frac{\sqrt{A}}{\sqrt{\phi}} \tag{V.75}$$

[1] Keyes, F. G., *Proc. Nat. Acad. Sci.*, **3**, 323–330 (1917).

Therefore, a plot of v vs. $1/\sqrt{\phi}$ will also be linear; the slope is $\sqrt{A}$, and the intercept is l. From Eq. (V.73) a value of δ is calculated for the corresponding values of v and ψ; and since δ and v are related by the equation

$$\ln \delta = \ln \beta - \frac{\alpha}{v} \qquad (V.76)$$

a plot of $\ln \delta$ (or $\log_{10} \delta$) against $1/v$ is a straight line from which α and β are readily obtained. Thus all the constants of the equation are evaluated from the graphs of straight lines.

Beattie-Bridgeman Equation.—A somewhat more complex but exceedingly useful equation is that proposed by Beattie and Bridgeman,[1]

$$p = \frac{RT\left(1 - \frac{c}{vT^3}\right)}{v^2}\left[v + B_0\left(1 - \frac{b}{v}\right)\right] - \frac{A_0}{v^2}\left(1 - \frac{a}{v}\right) \qquad (V.77)$$

where a, A_0, b, B_0, and c are arbitrary constants to be evaluated from experimental data. All the constants except c are evaluated from straight lines in a manner similar to that used for the Keyes equation. The original paper must be consulted for details. The equation is remarkably accurate as long as its use is restricted to the ranges of conditions for which the constants were determined. Beattie and Bridgeman originally applied it to the data on 10 gases up to maximum pressures in the range from 100 to 200 atm. and to densities approaching the critical densities, and the average deviation of the calculated from the observed pressures was only 0.18 per cent. In other words, it probably represents these data within the experimental accuracy.

Let us next examine the equation from the standpoint of the criteria given earlier in this chapter. First rearrange the equation into the following form:

$$pv = RT + \frac{\beta}{v} + \frac{\gamma}{v^2} + \frac{\delta}{v^3} \qquad (V.78)$$

where β, γ, and δ are temperature functions as follows:

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2} \qquad (V.79)$$

$$\gamma = -RTB_0b + aA_0 - \frac{RB_0c}{T^2} \qquad (V.80)$$

$$\delta = \frac{RB_0bc}{T^2} \qquad (V.81)$$

This is known as the "virial" form of an equation of state.

[1] BEATTIE, J. A., and O. C. BRIDGEMAN, *Proc. Am. Acad. Arts. Sci.*, **63**, 229–308 (1928).

As $p \to 0$, $v \to \infty$, and all terms with v in the denominator will be negligible, and the equation reduces to the ideal-gas form

$$pv = RT$$

From Eq. (V.78), $\dfrac{RT}{p} - v = \alpha = -\dfrac{\beta}{pv} - \dfrac{\gamma}{pv^2} - \dfrac{\delta}{pv^3}$

As $1/v \to 0$, $pv \to RT$, and

$$\alpha = -B_0 + \frac{A_0}{RT} + \frac{c}{T^3}$$

Thus we see that α is not zero but a finite quantity and a function of the temperature, in agreement with the experimental facts.

Differentiating the equation of state with respect to p at constant T and putting $v = \infty$ or $p = 0$, we get

$$\lim_{\frac{1}{v} \to 0} \left[\frac{\partial(pv)}{\partial p} \right]_T = \frac{\beta}{RT} = B_0 - \frac{A_0}{RT} - \frac{c}{T^3} \qquad \text{(V.82)}$$

Upon setting this limit equal to zero, the resulting cubic in T has only one real root, and that is the Boyle-point temperature. When $T > T_{\text{Boyle}}$, the derivative is greater than 0 and vice versa.

Application of the criteria for a critical point [Eqs. (V.38) and (V.39)] leads to two simultaneous equations that appear to give a unique solution for temperature and volume (and therefore pressure, also), and hence this criterion is satisfied.

By differentiation of the equation of state, we find

$$\left(\frac{\partial^2 p}{\partial T^2} \right)_v = -\frac{6 \left\{ \dfrac{cR}{v^3} \left[v + B_0 \left(1 - \dfrac{b}{v} \right) \right] \right\}}{T^4} \qquad \text{(V.83)}$$

For most conditions of v and T, this is readily shown to be a small negative number, approaching zero (linear isometrics) as a limit as $T \to \infty$ at all volumes or as $1/v \to 0$ at all temperatures.

Thus we see that the Beattie-Bridgeman equation very satisfactorily meets the important criteria imposed on any equation of state by the known behavior of gases.

In Table V.4 there are given the values of constants for this equation insofar as they have been determined for various gases.

It should be emphasized that the equation cannot be expected to be accurate if it is used outside the ranges for which the constants were determined. For example, if the first equation for nitrogen, which was based on a maximum pressure of 134 atm., is extrapolated to 1,000 atm. at 0°C., it is found to be only a rough approximation, not much better than van der Waals' equation. The best guide to follow in any given

TABLE V-4.—CONSTANTS OF THE BEATTIE-BRIDGEMAN EQUATION OF STATE
(Units: atm., liters, g.-moles, °K. $R = 0.08206$)

Gas	A_0	a	B_0	b	$c \times 10^{-4}$	Temp. range, °C.	Maximum pressure, atm.	Minimum volume, cc./g.-mole	Lit. ref.
He	0.0216	0.05984	0.01400	0 0	0.0040	400 to −252	102	100	1
Ne	0.2125	0.02196	0.02060	0.0	0 101	400 to −217	106	118	1
A	1.2907	0 02328	0 03931	0.0	5 99	400 to −150	114	167	1
H₂	0.1975	−0.00506	0.02096	−0.04359	0.0504	200 to −244	103	100	1
H₂ (below critical density)	0 12404	0 05618	0.02022	−0.00722	2.00	300 to − 70	1,000	65	6
H₂ (above critical density)	0.12404	0 05618	0.01750	−0.01968	2.00	300 to − 70	1,000	37	6
N₂	1.3445	0.02617	0 05046	−0.00691	4.20	400 to −149	134	182	1
N₂*	1.2517	0 01866	0.04603	−0 02587	6.16	400 to − 70	1,000	84	5
O₂	1 4911	0.02562	0 04624	0 004208	4.80	100 to −117	103	111	1
Air	1 3012	0 01931	0 04611	−0.01101	4 34	200 to −145	177	125	1
CO₂	5 0065	0.07132	0.10476	0 07235	66.00	100 to 0	111	182	1
CH₄	2.2769	0 01855	0.05587	−0.01587	12.83	200 to 0	243	167	
(C₂H₅)₂O	31 278	0.12426	0.45446	0.11954	33 33	325 to 150	90	370	1
C₂H₄	6 1520	0.04964	0.12156	0.03597	22.68	200 to 0	286	125	2
NH₃	2 3930	0.17031	0.03415	0.19112	476.87	325 to − 35	130	340	3
CCl₂F₂	23 7	0.305	.59	0.622		126 to 30	18.5	1,430	4
C₂H₆	5 8800	0.05861	0.09400	0.01915	90.00	25 to 250	193	200	7
C₃H₈	11.9200	0.07321	0.18100	0.04293	120.00	97 to 275	305	100	8
n-C₄H₁₀	17.7940	0.12161	0.24620	0.09423	350.00	150 to 300	118	280	9
n-C₇H₁₆	54.520	0.20066	0.70816	0.19179	400.00	275 to 350	315	200	10
Iso-C₄H₁₀	16.9600	0.10860	0.24200	0.08750	250.00	150 to 250	250	111	11
CH₃OH	33.309	0.09246	0.60362	0.09929	32.031				12

NOTE: The constants for N_2 can be used for CO and the CO_2 constants for N_2O at moderate pressures and temperatures not too near the critical ones.

* Somewhat better agreement was obtained by adding a sixth constant a', making the last term of Eq. (V.77): $1 - (a/v) - (a'/v^2)$. The difference does not seem great enough to warrant the additional complication.

[1] BEATTIE, J. A., and O. C. BRIDGEMAN, Proc. Am. Acad. Arts Sci., 63, 229–308 (1928).
[2] GILLESPIE, L. J., J. Phys. Chem., 33, 354–360 (1929).
[3] BEATTIE, J. A., and C. K. LAWRENCE, J. Am. Chem. Soc., 52, 6–14 (1930).
[4] BUFFINGTON, R. M., and W. K. GILKEY, Ind. Eng. Chem., 23, 254 (1931).
[5] DEMING, W. E., and L. E. SHUPE, J. Am. Chem. Soc., 52, 1382–1389 (1930).
[6] DEMING, W. E., and L. E. SHUPE, J. Am. Chem. Soc., 53, 843–849 (1931).
[7] BEATTIE, J. A., C. HADLOCK, and N. POFFENBERGER, J. Chem. Phys., 3, 93–96 (1935).
[8] BEATTIE, J. A., W. C. KAY, and J. KAMINSKY, J. Am. Chem. Soc., 59, 1589–1590 (1937).
[9] BEATTIE, J. A., G. L. SIMARD, and G. SU, J. Am. Chem. Soc., 61, 26–27 (1939).
[10] SMITH, L. B., J. A. BEATTIE, and W. C. KAY, J. Am. Chem. Soc., 59, 1587–1589 (1937).
[11] BEATTIE, J. A., H. G. INGERSOLL, and W. H. STOCKMAYER, J. Am. Chem. Soc., 64, 548 (1942).
[12] BEATTIE, J. A., and W. H. STOCKMAYER, Reports on Progress in Physics, 7, 195 (1940).

case is the molal volume (or the density). The equations will not, in general, be accurate if used in any region where the molal volume is less than the minimum listed in Table V.4.

Unlike most of the other equations referred to, the Beattie-Bridgeman equation does not demand that the isometrics be linear. If, however,

the constant c is put equal to zero, it reduces to a simpler linear isometric form that may be useful in special cases.   One such case is that of the refrigerant dichlorodifluoromethane, the constants for which are given in Table V.4.   The equation in this form has also been applied to the data on three other fluorochloromethanes and one fluorochloroethane.[1]

Deming and Shupe[2] have applied the Beattie-Bridgeman equation to nitrogen and hydrogen over a wider range of conditions than those chosen by Beattie and Bridgeman in their test of the equation, and their constants are also included in Table V.4.   By introducing a sixth arbitrary constant they succeeded in reproducing the observed pressures of nitrogen to a maximum deviation of 1.4 per cent down to a reduced volume of about 0.94.   At higher densities the agreement was much poorer, the deviation being as much as 43 per cent in one case.   In the case of hydrogen, they were able to extend the range of usefulness of the equation by using a different set of constants above and below the critical density (0.0154 g.-mole per cc.).

Maron and Turnbull[3] have developed a method for determining the constants of the Beattie-Bridgeman equation for any gas from the critical data for that gas and the equation of state constants for a reference gas.   The method is based on the assumption that all gases have the same activity coefficient at the same reduced pressure and temperature.   It is therefore essentially an application of the law of corresponding states, leading to an algebraic rather than a graphical result.

In using either the Keyes or the Beattie-Bridgeman equation, the volume must be obtained by a trial process exactly similar to that outlined for the case of the van der Waals' equation.

Beattie Equation.—Beattie[4] has rearranged the Beattie-Bridgeman equation to the following explicit-volume type:

$$v = (\pi + B)(1 - \epsilon) - \frac{A}{RT} \tag{V.84}$$

where
$$A = A_0\left(1 - \frac{a}{\pi}\right)$$

$$B = B_0\left(1 - \frac{b}{\pi}\right)$$

$$\epsilon = \frac{c}{\pi T^3}$$

$$\pi = \frac{RT}{p}$$

[1] Benning, A. F., and R. C. McHarness, *Ind. Eng. Chem.*, **32**, 698–701 (1940).

[2] Deming, W. E., and L. E. Shupe, *J. Am. Chem. Soc.*, **52**, 1382 (1930); **53**, 843 (1931).

[3] Maron, S. H., and D. Turnbull, *Ind. Eng. Chem.*, **33**, 408 (1941).

[4] Beattie, J. A., *Proc. Nat. Acad. Sci.*, **16**, 14–19 (1930).

The constants are the same as for the Beattie-Bridgeman equation, and the same numerical values may be used.   The equation is not so accurate as the Beattie-Bridgeman equation, but the agreement with observed data is quite good if its use is restricted to states well above the critical region and to densities well below the critical density.   The reason for giving a less accurate variant of the Beattie-Bridgeman equation is that an explicit volume equation is more convenient for certain calculations.

GAS MIXTURES

In practically all industrial applications one has to deal with mixtures of fluids rather than one pure fluid.   It is important, therefore, to see how the ideas and relationships for pure gases might be generalized to cover the more complex case of mixtures.   We may say at the very start that the situation is far from satisfactory since comparatively little work has been done on mixtures.   It will be our purpose in this chapter to review what information is now available, realizing as we go along that the picture is very incomplete and can be sketched only in rough outline.

The term "mixture" will be understood to mean a molecularly homogeneous mixture, *i.e.*, a true solution.   Methods of expressing the composition of solutions have already been discussed in Chap. I.   Some mixtures of great industrial importance, such as many that are encountered in petroleum refining, are so complex that their composition cannot be stated in any simple terms.   Such mixtures would have to be characterized by some properties that they possess rather than by any statement of the chemical individuals present.

When the composition of a mixture is known, the ideal way to express its pvT behavior is in terms of the known behavior of the pure components.   Thus, if one has an equation of state for each component in the mixture, the simplest way to describe the behavior of the mixture would be by means of some combination of the constants of the equations for the components.   Unfortunately, this ideal goal is still far in the future, but some significant progress has been made in this direction.

Mixtures of Ideal Gases.—From the kinetic picture of an ideal gas, it is clear that a mixture of ideal gases would behave in the same manner, as far as pvT changes are concerned, as a single pure gas.   Since the underlying idea of the ideal gas is that the individual molecules exert no attractive forces on one another and that it makes no difference whether the molecules are substance A or substance B, it is obvious that it also makes no difference whether a given molecule of A is surrounded by other A molecules or whether the place of some of the A's has been taken by B's, C's, etc.   In other words, each gas in a mixture of ideal gases behaves as if it were alone in the given volume.

Let us consider a mixture of three ideal gases A, B, and C confined in a vessel of volume V at total pressure p and temperature T on the absolute scale.   Let N_A, N_B, and N_C be the respective number of moles. Each gas, if it occupied the volume alone at the same temperature, would exert a definite pressure, less than p, and calculable from the ideal-gas law.   Thus, we may write

$$\begin{aligned} p_A V &= N_A RT \\ p_B V &= N_B RT \\ p_C V &= N_C RT \end{aligned} \qquad \text{(V.85)}$$

Now, if the mixture is ideal,

$$pV = NRT \qquad \text{(V.86)}$$
$$\therefore p = p_A + p_B + p_C \qquad \text{(V.87)}$$

Dividing any one of Eqs. (V.85) by Eq. (V.86), one gets

$$\frac{p_i}{p} = \frac{N_i}{N} = x_i$$

or
$$p_i = x_i p \qquad \text{(V.88)}$$

The pressure p_i defined by this equation is known as a "partial pressure" and will henceforth be represented by the symbol $\bar{p}_i$.   On this basis we may rewrite Eq. (V.87) in the form

$$p = \bar{p}_A + \bar{p}_B + \bar{p}_C \qquad \text{(V.89)}$$

This equation is true for any number of components, always provided that the entire mixture can be regarded as an ideal gas.   The fact expressed by Eq. (V.87) is known as the "law of additive pressures" or as "Dalton's law," and Eq. (V.89) is a special case applying only to a mixture of ideal gases.

The term "partial pressure" has frequently been used rather loosely and without exact definition, and this leads to much confusion when one is dealing with gas mixtures that are not ideal.   We shall always define this quantity by means of Eq. (V.88).

Let us next consider three ideal gases, all at the same pressure p, but of different molal mass so that the volumes will be different; then we can write

$$\begin{aligned} pV_A &= N_A RT \\ pV_B &= N_B RT \\ pV_C &= N_C RT \end{aligned} \qquad \text{(V.90)}$$

Now let the three gases be mixed while the temperature and total pressure are kept constant.   The mixture must also be ideal, and we can write Eq. (V.86) for it.   Adding Eqs. (V.90) and comparing with Eq. (V.86),

we see that

$$V = V_A + V_B + V_C \tag{V.91}$$

In other words, for ideal gases the volumes are additive at constant temperature and pressure. It should be noted that the volumes in Eq. (V.91) are the total volumes for the number of moles in question. In terms of *molal volume* the equation becomes

$$v = v_A x_A + v_B x_B + v_C x_C \tag{V.92}$$

This law of additive volumes is also known as Amagat's law or Leduc's law. Analogous to partial pressure, one may define a partial volume by equation

$$V_i = x_i V \tag{V.93}$$

By analogy to the case of a single ideal gas, we may write for any mixture of ideal gases

$$p = \frac{m}{M_{av}} \frac{RT}{V} \tag{V.94}$$

where M_{av} is the average molecular weight of the gas and m is the total weight of all the components. Comparing Eqs. (V.94) and (V.86),

$$M_{av} = \frac{m}{N} = \frac{M_A N_A}{N} + \frac{M_B N_B}{N} + \frac{M_C N_C}{N} + \cdots \tag{V.95}$$

or $\qquad M_{av} = x_A M_A + x_B M_B + x_C M_C + \cdots \tag{V.96}$

By Eqs. (V.94) and (V.96) a complex mixture of constant composition may be treated as if it were a single pure gas whose molecular weight is the average molecular weight of the mixture.

Illustration 5.—Calculate the density at 80°F. and 20 lb. per sq. in. absolute pressure, of a gas whose composition, in volume per cent, is as follows: 50.0 per cent H_2, 30.0 per cent N_2, 18.0 per cent CO_2, 2.0 per cent H_2O.

$$M_{av} = 0.500 \times 2.016 + 0.300 \times 28.00 + 0.18 \times 44.00$$
$$+0.020 \times 18.00 = 17.69$$

$$\text{Density} = \frac{m}{V} = \frac{pM_{av}}{RT} \qquad \text{[By Eq. (V.94)]}$$

$$R \text{ in these units} = 10.73$$

$$\text{Density} = \frac{20 \times 17.69}{10.73 \times 539.6} = 0.0611 \text{ lb./cu. ft.}$$

Note that we have tacitly assumed that the per cent by volume of a gas equals the mole per cent. This is strictly true for ideal gases as may be seen by dividing any one of Eqs. (V.90) by (V.86), giving

$$\frac{V_i}{V} = \frac{N_i}{N} \tag{V.97}$$

This is not true, in general, for any but ideal gases.

Law of Additive Pressures.—We may still assume a law of additive pressures (Dalton's law) even though the gases are not ideal. Thus, for the mixing of gases at constant volume and temperature we may write

$$p = p_A + p_B + p_C + \cdots \qquad (V.98)$$

p_A, p_B, etc., in this case stand for the pressures that the individual gases A, B, etc., exert when occupying alone the total volume at the given temperature. These pressures should not be referred to as partial pressures because they do not, in general, bear the relation to the total pressure demanded by Eq. (V.88), which we have agreed to adopt as our definition of partial pressure.

For the special case where the pvT behavior of each individual gas can be represented by an equation of state of the explicit pressure form, Eq. (V.98) can be written

$$p = \phi_1(v,T,x_A) + \phi_2(v,T,x_B) + \cdots \qquad (V.99)$$

where $\phi(v,T,x_i)$ is an equation of state, in the explicit-pressure form, of a given pure component occupying the molal volume of the mixture at the same temperature as the mixture. Even if the equations of state of the individual gases were available in the explicit-volume form, the additive-pressure law as expressed by Eq. (V.98) can still be applied but the application is less convenient because a trial solution for the individual pressures would be required. For an ideal gas, $\phi(v,T,x_i)$ has the form $x_i RT/v$. If the individual gases obey the van der Waals' equation, we have, for any gas,

$$p_i = \frac{N_i RT}{V - N_i b_i} - \frac{N_i^2 a_i}{V^2} \qquad (V.100)$$

where V is the total volume. This results directly from Eq. (V.43) by substitution of

$$v_i = \frac{V}{N_i}$$

If the total number of moles of the mixture is unity, then Eq. (V.100) becomes

$$p_i = \frac{x_i RT}{v - x_i b_i} - \frac{x_i^2 a_i}{v^2} \qquad (V.101)$$

where v is now the molal volume of the mixture. The right-hand side of Eq. (V.101) is the $\phi(v,T,x_i)$ as required for Eq. (V.99), and substituting in Eq. (V.99) one gets

$$p = RT\left(\frac{x_A}{v - x_A b_A} + \frac{x_B}{v - x_B b_B} + \cdots\right) - \frac{1}{v^2}\left(a_A x_A^2 + a_B x_B^2 + \cdots\right) \qquad (V.102)$$

where a_A and b_A are the van der Waals' constants for component A. Similar equations may be obtained by combining any equation of state explicit in p with Eq. (V.98).

Another form of the additive-pressure law[1] can be written as follows:

$$p = x_A p_A + x_B p_B + \cdots \qquad (V.103)$$

where p_A, p_B, $\cdots$ are the pressures that would be exerted by the individual components at the temperature of the mixture and at a molal volume identical with that of the mixture. The two statements of the additive-pressure law given by Eqs. (V.98) and (V.103) are identical for ideal gases but not for actual ones. For example, if the individual gases obey the van der Waals' equation, one gets (using Eq. V.103)

$$p = RT \left(\frac{x_A}{v - b_A} + \frac{x_B}{v - b_B} + \cdots \right) - \frac{1}{v^2} (a_A x_A + a_B x_B + \cdots) \quad (V.104)$$

which is not the same as Eq. (V.102).

Law of Additive Volumes.—In an analogous fashion we may generalize Amagat's additive-volume law and write Eqs. (V.91) and (V.92) for cases where the mixture is not an ideal gas. This is merely a special case of the concept of an ideal solution, which was developed in the preceding chapter. The volumes of the individual components are, of course, referred to the pressure and temperature of the mixture. We may put Eq. (V.92) in the form

$$v = x_A \psi_1(p,T) + x_B \psi_2(p,T) + \cdots \qquad (V.105)$$

where $\psi(p,T)$ is an equation of state in the explicit-volume form for a given pure component at the total pressure p and the temperature of the mixture and v is the molal volume of the mixture. For the ideal-gas mixture, $x_i \psi(p,T)$ has the form $x_i RT/p$. For real gases we may use any equation of the explicit-volume form such as Eq. (V.84).

A few numerical illustrations of these equations for gas mixtures will now be given both to show how they are used and to indicate the agreement with experiment.

Illustration 6.—250 cu. ft. of a gas mixture containing 75 mole per cent hydrogen and 25 mole per cent nitrogen, at a pressure of 14.7 lb. per sq. in. abs. and a temperature of 50°F. is to be compressed into an evacuated cylinder of 1.000 cu. ft. volume. If the temperature of the gas after compression into the cylinder is 122°F. (50°C.), what pressure in atmospheres would be developed?

Let us compare the following ways of calculating this pressure with the experimental results of Bartlett, Cupples, and Tremearne:[2]

[1] This will be called the Bartlett additive-pressure law, since it appears to have been first used by E. P. Bartlett and coworkers.

[2] Bartlett, E. P., H. L. Cupples, and T. H. Tremearne, *J. Am. Chem. Soc.*, **50**, 1275 (1928).

1. Ideal-gas law.
2. Combination of law of additive pressures [Eq. (V.98)] and the van der Waals' equation.
3. Combination of law of additive volume and the van der Waals' equation.
4. Law of additive pressure [Eq. (V.98)] and Beattie-Bridgeman equation of state.
5. Law of additive volumes and Beattie-Bridgeman equation.

The experimental data are given in terms of the compressibility factor A, as a function of pressure at constant temperature. For 50°C., some of the tabulated values are as follows:

p_{atm}	1	50	100	200	300	400
A	1.1831	1.2144	1.2495	1.3282	1.4034	1.4862

Interpolation can be made from a graph; but since the relationship is approximately linear over the range in which we are interested, linear interpolation between tabulated values will be used. Assuming the ideal-gas law to apply at the 1 atm. state,

$$N = \frac{pv}{RT} = \frac{14.70 \times 250}{10.73 \times 510} = 0.671 \text{ lb.-mole}$$

At the high pressure,

$$\text{Molal volume } v = \frac{1.000}{0.671} = 1.490 \text{ cu. ft.}$$

From the definition of A,

$$p = \frac{p_1 v_1}{v} A = \frac{359A}{v}$$

For this special case,

$$p = \frac{359A}{1.490} = 240.8A$$

The solution may now be made by a simple trial process as follows:
Assume $p = 300$; then $A = 1.4034$; $p_{(calc.)} = 338$.
Assume $p = 350$; then $A = 1.4448$; $p = 348$.
The correct value lies between these two and much closer to the larger value. One or two more trials shows that $p = 348$ atm. (closely enough). This we may call the observed value.

1. $p = \dfrac{NRT}{v} = \dfrac{0.671 \times 0.730 \times 582}{1.000} = 285$ atm.

2. The van der Waals' constants for the two gases are given in Table IV in the Appendix.

Substituting values in Eq. (V.102),

$$p = 0.730 \times 582 \left(\frac{0.750}{1.490 - 0.750 \times 0.426} + \frac{0.250}{1.490 - 0.250 \times 0.618} \right)$$
$$- \frac{1}{(1.49)^2} [62.80(0.750)^2 + 346(0.250)^2]$$

$$= 326.0 \text{ atm.}$$

3. By Eq. (V.92) we have

$$1.49 = 0.75 v_{H_2} + 0.25 v_{N_2}$$

or
$$v_{H_2} = 1.988 - 0.333v_{N_2}$$

The solution consists in taking trial values of v_{N_2}, obtaining v_{H_2} from this equation, and then calculating the pressure for each gas from the van der Waals' equation. The criterion of correct trial values is equality of the pressures for the two gases.

For example, assume
$$v_{N_2} = 1.500 \text{ cu. ft./lb.-mole}$$
then
$$v_{H_2} = 1.488 \text{ cu. ft./lb.-mole}$$

The pressures calculated from van der Waals are
$$p_{N_2} = 328 \text{ atm.}$$
$$p_{H_2} = 372 \text{ atm.}$$

After a few more trials, the following values are chosen as sufficiently close to the correct ones:
$$v_{N_2} = 1.410$$
$$v_{H_2} = 1.510$$
From these values,
$$p_{N_2} = 363$$
$$p_{H_2} = 364$$

The desired total pressure is 363.5 atm.

4. The molal volumes of the individual gases per cubic foot of the mixture are

$$\frac{1.00 \times 28.3}{0.75 \times 0.671 \times 453.6} = 0.124 \text{ liter} \qquad \text{(for } H_2\text{)}$$
$$3 \times 0.124 = 0.372 \text{ liter} \qquad \text{(for } N_2\text{)}$$

Substituting these values in the Beattie-Bridgeman equation using the constants of Deming and Shupe as given in Table V.4, we find

$$p_{H_2} = 246.5$$
$$p_{N_2} = 70.9$$

The pressure of the mixture $= 317.4$ atm.

5. The procedure is the same as in the case of part 3. The final results of the trial solution are
$$v_{H_2} = 0.0932 \text{ liter/g.-mole}$$
$$v_{N_2} = 0.0924 \text{ liter/g.-mole}$$
$$p = 343.5 \text{ atm.}$$

From these various methods of calculating the pressure one would conclude that any one of these methods of calculation is superior to the use of the ideal-gas law and that the additive-volume law gives somewhat better results for this particular system than the additive-pressure law.

Compressibility Factor of Gas Mixtures.—One may define a compressibility factor for a mixture just as for a single pure gas by the equation

$$pv = C_m RT \qquad \text{(V.106)}$$

C_m is a function not only of p and T but also of the composition of the mixture. For a given composition one could prepare and use com-

pressibility charts just as is done for a single component. To present in this way the behavior of all mixtures of only two components would lead to considerable complication, and in the majority of cases the data would not be available anyway. As a first approximation one might assume a simple mixture law as given by the following equation:

$$C_m = x_A C_A + x_B C_B + \cdots \qquad (V.107)$$

If C_m, C_A, C_B, etc., all refer to the same temperature and total pressure, then, from Eq. (V.107) and the definition of the compressibility factor,

$$\frac{pv_m}{RT} = x_A \frac{pv_A}{RT} + x_B \frac{pv_B}{RT} + \cdots \qquad (V.108)$$

or $$v_m = x_A v_A + x_B v_B + \cdots \qquad (V.109)$$

In other words, this method of combining compressibility factors is based on the application of the additive-volume law. If, on the other hand, the factors are those for the mixture and the individual components at the same temperature and all at the same total volume, we have

$$C_i = \frac{p_i v_i}{RT}$$

and since $$v_i = \frac{v_m}{x_i}$$

then $$C_i = \frac{p_i v_m}{x_i RT}$$

Substituting in Eq. (V.107),

$$p_m = p_A + p_B + \cdots \qquad (V.110)$$

In other words, this method of combining the compressibility factors is based on the additive-pressure law. Similarly, it can be shown that, if the compressibility factors of the components are taken at the same temperature and molal volume as the mixture, then one also obtains Eq. (V.107). Therefore, this equation can be used to represent three different additive laws, depending on how the compressibility factors of the individual components are obtained.

The same methods of combination are applicable to the other compressibility factor, A, and it can be shown that they also imply the additive-volume and additive-pressure laws provided that the ideal-gas law may be assumed for the standard pressure p_1.

The use of the generalized compressibility-factor chart combined with either the additive-volume or the additive-pressure law gives a relatively simple way to deal with a gas mixture. To illustrate, we shall continue with Illustration 6 (page 191).

Illustration 6 (continued).

6. Use of additive-volume law and generalized compressibility-factor chart.

Reduced pressures and temperatures, from the critical data in Table IV in the Appendix are as follows:

$$T_R = \frac{273 + 50}{33.2 + 8} = 7.84 \qquad \text{(for } H_2\text{)}$$

$$p_R = \frac{p}{12.8 + 8} = \frac{p}{20.8}$$

$$T_R = \frac{273 + 50}{126} = 2.56 \qquad \text{(for } N_2\text{)}$$

$$p_R = \frac{p}{33.5}$$

Since the pressure is unknown, a trial solution must be used. Assume $p = 350$.

$$p_R(H_2) = 16.8; \qquad p_R(N_2) = 10.44$$

From the compressibility-factor chart (Fig. V.3),

$$C_{H_2} = 1.21; \qquad C_{N_2} = 1.18$$

Substituting in Eq. (V.107),

$$C_m = 0.75(1.21) + 0.25(1.18) = 1.204$$

Then, from Eq. (V.106),

$$p = \frac{1.204 \times 1.3145 \times 323}{1.490} = 343$$

This result is so close to the assumed value that further trials are scarcely necessary. A somewhat closer agreement is obtained with $p = 340$ atm., and this will be taken as the solution.

7. Use of additive-pressure law and generalized compressibility-factor chart.

Let us first assume that the Dalton additive-pressure law is to be used. Then the molal volumes will be as follows:

$$v_m = 1.490; \qquad v_{H_2} = \frac{1.490}{0.75} = 1.985; \qquad v_{N_2} = \frac{1.490}{0.25} = 5.960$$

The solution would be very simple if a generalized chart in terms of v_R and T_R were available. The use of Figs. V.2 and V.3 will require a short trial process to obtain the compressibility factor.

$$C_{H_2} = \frac{p_{H_2}v_{H_2}}{RT} = \frac{1.985p_{H_2}}{1.3145 \times 323} = 0.00468p_{H_2}$$

Assume $p_{H_2} = 250$, $p_R = 250/20.8 = 12.0$. From Fig. V.3, at $T_R = 7.84$ and $p_R = 12.0$, $C = 1.105$. But

$$C = 0.00468 \times 250 = 1.170$$

With a few more trials, p_{H_2} is found to be 234.

$$C_{N_2} = \frac{p_{N_2}v_{N_2}}{RT} = \frac{5.960p_{N_2}}{1.3145 \times 323} = 0.01403p_{N_2}$$

By a trial process similar to that used for H_2,

$$p_{N_2} = 72$$
$$\text{Total pressure} = 234 + 72 = 306 \text{ atm.}$$

If we assume Bartlett's form of the additive-pressure law, then

$$C_m = C_A x_A + C_B x_B$$

where C_A and C_B are the compressibility factors of the components at the molal volume of the mixture, 1.490 cu. ft., and at 50°C. Thus,

$$C_A = \frac{1.49 p_A}{1.3145 \times 323} = .00351 p_A$$

Likewise, $C_B = 0.00351 p_B$
or since $p = p_c p_R$
we have $C_A = 0.0730 p_{RA}$ (hydrogen)
                   $C_B = 0.1175 p_{RB}$ (nitrogen)

By drawing these equations as straight lines on the C vs. p_R graph and finding the intersection with the reduced isotherms, we find

$$C_A = 1.205, \qquad C_B = 1.19$$
$$\therefore C_m = 0.75 C_A + 0.25 C_B = 1.202$$
$$p = \frac{C_m R T}{v}$$
$$= \frac{1.202 \times 1.3145 \times 323}{1.49}$$
$$= 343 \text{ atm.}$$

Combination of Constants of Equations of State.—It has been demonstrated both experimentally and from theoretical considerations that the equations of state used for single gases can also be applied to mixtures. With experimental data on a given mixture the constants can be determined in the same manner as for a pure gas. Since experimental data on mixtures are very meager, it is most desirable to have some means of combining the constants for the individual gases to obtain constants for the mixture to use in the same equation of state.

In the case of a binary mixture it has been assumed on the basis of kinetic theory that a constant for the mixture is related to the constants for the individual gases by the equation

$$k_m = k_A x_A^2 + 2 k_{AB} x_A x_B + k_B x_B^2 \qquad (V.111)$$

where k_{AB} is a so-called "interaction constant." Several methods have been proposed for evaluating the interaction constant, the two simplest being

$$k_{AB} = \frac{k_A + k_B}{2} \qquad (V.112)$$

and $$k_{AB} = \sqrt{k_A k_B} \qquad (V.113)$$

or the arithmetic mean and geometric mean, respectively, of the indi-

vidual constants. Combination of Eqs. (V.112) and (V.113) with Eq. (V.111) leads, respectively, to

$$k_m = k_A x_A + k_B x_B \tag{V.114}$$

and
$$k^{\frac{1}{2}}_m = k^{\frac{1}{2}}_A x_A + k^{\frac{1}{2}}_B x_B \tag{V.115}$$

The method of combination given by Eq. (V.114) is commonly referred to as "linear" and that by Eq. (V.115) as "linear square root." One other method, known as the "Lorentz combination," has been used to a considerable extent and should be mentioned. According to this method,

$$k^{\frac{1}{2}}_{AB} = \tfrac{1}{2}(k^{\frac{1}{2}}_A + k^{\frac{1}{2}}_B) \tag{V.116}$$

which, combined with Eq. (V.111), gives

$$k_m = k_A x_A^2 + \tfrac{1}{4}(k^{\frac{1}{2}}_A + k^{\frac{1}{2}}_B)^3 x_A x_B + k_B x_B^2 \tag{V.117}$$

Beattie and Ikehara[1] have made a thorough study of the methods of combining the constants, and they find that the best procedure is to use the linear combination for all constants having the dimension of volume to the first power and linear square root for those having dimensions of volume squared. Thus the a of van der Waals would be combined by linear square root [Eq. (V.115)] and the b by Eq. (V.114). In the case of the Beattie-Bridgeman equation, this would be linear square root for A_0 and linear combination for all the others. This method was tested, using the Beattie-Bridgeman equation, on the following mixtures: argon-ethylene, oxygen-ethylene, nitrogen-hydrogen, nitrogen-methane, and hydrogen–carbon monoxide. In all cases the data were represented satisfactorily and in most cases within the experimental accuracy. The agreement was much better than that obtained either with the law of additive volumes or with the additive-pressure law.

Deming and Shupe[2] applied the Beattie-Bridgeman equation to Bartlett's data on a 3 to 1 H_2-N_2 mixture and were able to represent them satisfactorily by using two sets of constants, one for densities above critical (about 0.0135 g.-mole per cc.) and the other for densities below. Constants for the mixture derived from those of the individual components gave good representation up to a density of 0.0070 g.-mole per cc. Contrary to the findings of Beattie and Ikehara they found that linear square root combination for B_0 gave better results than linear combination.

The general equation of state, of the Beattie-Bridgeman form, may be written for any mixture as follows:

$$p = \frac{RT(1 - \epsilon)}{v^2} (v + B) - \frac{A}{v^2} \tag{V.118}$$

[1] BEATTIE, J. A., and S. IKEHARA, *Proc. Am. Acad. Arts Sci.*, **64**, 127–176 (1930).
[2] DEMING, W. E., and L. E. SHUPE, *J. Am. Chem. Soc.*, **53**, 860–869 (1931).

where

$$A = (\Sigma x_i \sqrt{A_{0_i}})^2 \left(1 - \frac{\Sigma x_i a_i}{v}\right)$$

$$B = \Sigma x_i B_{0_i} \left(1 - \frac{\Sigma x_i b_i}{v}\right)$$

$$\epsilon = \frac{\Sigma x_i c_i}{v T^3}$$

$$(\Sigma x_i \sqrt{A_{0_i}})^2 = A_{0_m} = (x_A \sqrt{A_{0_A}} + x_B \sqrt{A_{0_B}} + \cdots)^2$$

$$\Sigma x_i a_i = a_m = x_A a_A + x_B a_B + \cdots$$

with similar expressions for $\Sigma x_i B_{0_i}$, $\Sigma x_i b_i$, and $\Sigma x_i c_i$. This equation is based on molal volume; but if one wishes to use total volume, it is necessary only to replace x_i by N_i and add N in front of RT.

Illustration 6 (continued).

8. Combination of the constants of the Beattie-Bridgeman equation of state.

Using the Deming and Shupe constants, linear square root combination for A_0, and linear combination for the other constants, we have

$$(\Sigma x_i \sqrt{A_{0_i}})^2 = (0.75 \sqrt{0.12404} + 0.25 \sqrt{1.2517})^2 = 0.29576$$

$$\Sigma x_i a_i = 0.75(0.05618) + 0.25(0.01866) = 0.04680$$

$$\Sigma x_i B_{0_i} = 0.75(0.02022) + 0.25(0.04603) = 0.02668$$

$$\Sigma x_i b_i = 0.75(-0.00722) + 0.25(-0.02587) = -0.01189$$

$$\Sigma x_i c_i = 0.75(2.00 \times 10^4) + 0.25(6.16 \times 10^4) = 3.04 \times 10^4$$

$$A = 0.14686$$

$$B = 0.030092$$

$$\epsilon = 0.0000969$$

$$R = 0.08206$$

Substituting the values of these constants and $v = 0.09296$ in Eq. (V.118),

$$p = 360.5 \text{ atm.}$$

Gilliland[1] proposed a method for treating the compressibility of gas mixtures that is based on the use of an equation of state of the linear isometric form and on various schemes for combining the constants. For example,

$$p_m = \phi_m T - \psi_m \tag{V.119}$$

where ϕ and ψ are functions of volume only, and

$$\frac{1}{\phi_m} = \frac{1}{\phi_A} x_A + \frac{1}{\phi_B} x_B + \cdots \tag{V.120}$$

$$\phi_m = \phi_A x_A + \phi_B x_B + \cdots \tag{V.121}$$

$$\psi_m = \psi_A x_A + \psi_B x_B + \cdots \tag{V.122}$$

$$\psi_m = (x_A \sqrt{\psi_A} + x_B \sqrt{\psi_B} + \cdots)^2 \tag{V.123}$$

The constants for the individual gases are to be taken at the temperature and molal volume of the mixture. Four different equations of state for the mixture result from various combinations of Eqs. (V.120) to (V.123)

[1] GILLILAND, E. R., *Ind. Eng. Chem.*, **28**, 212–215 (1936).

with Eq. (V.119). Gilliland tested all four of these methods on compressibility data and found that the combination of constants by means of Eqs. (V.121) and (V.123), which he terms "additivity of intrinsic pressures," gave the best results. This method was better than the use of either the additive-volume or the additive-pressure law. Though the method appears to give accurate results, it is rather cumbersome to use, and some of the other methods given in this chapter are more convenient if one has only a few calculations to make.

Beattie and Stockmayer[1] have recently given an excellent review of equations of state for both pure gases and gas mixtures.

Agreement of Mixture Laws with Experiment.—So little work, relatively speaking, has been done on mixtures that it is difficult to make any general statements about the applicability of the various mixture laws. We are probably safe in making the statement that almost any one of the methods discussed for dealing with gas mixtures is more accurate than assuming the ideal-gas law.

For mixtures of gases that are well above the critical temperature such as nitrogen-hydrogen around room temperature, the additive-volume law appears to be quite accurate. For example, all the data of Bartlett and coworkers on the H_2-N_2 system can be reproduced by the additive-volume law with an accuracy of 2 per cent or better. The additive-pressure law as expressed by Eq. (V.98) is considerably less accurate. On the other hand, the special form of this law given by Eq. (V.103) was shown by Bartlett to be as good as the additive-volume law for one N_2-H_2 mixture. However, this rule has been so little tested that one cannot generalize about it.

When one of the components is above but close to its critical temperature, the additive-pressure law appears to be the more accurate if we can generalize the results obtained by Masson and Dolley[2] on the systems argon-ethylene and oxygen-ethylene. The maximum deviation from the pressure law was about 9 per cent as compared with 32 per cent from the volume law.

An equation of state for the mixture with constants obtained by suitable combination of the constants for the pure components is prob ably the most accurate of any of the methods for the two general cases just mentioned.

When the temperature is below the critical temperature of one or more components, then all the various mixture rules break down because one or more of the components cannot exist as a vapor in the pure state above the vapor pressure. Practically no work has been done on this

[1] BEATTIE, J. A., and W. H. STOCKMAYER, Reports on Progress in Physics, *Phys. Soc.*, **7**, 195 (1940).

[2] MASSON, I., and L. G. DOLLEY, *Proc. Roy. Soc. (London)*, **103A**, 524 (1923).

case and hence no definite statements can be made, but one possible approach is to combine the constants of an equation of state even though one (or more) of the components does not exist as a vapor at the total pressure of the mixture. More experimental data for this case are desirable in order to test this and other possible methods of calculation.

Use of Reduced Coordinates.—This method proved so useful in the case of pure components that it was soon tried for mixtures. When the true critical point of the mixture is used for calculating the reduced coordinates, the curves deviate considerably from those for pure components, especially in the critical region.[1] Given the experimental data on a mixture, obviously a fictitious value of the critical pressure and temperature can be chosen so that the compressibility-factor curves for the mixture in terms of reduced coordinates will coincide with those for pure components. This point was termed the "pseudocritical point" by Kay,[2] who calculated it for a number of complex petroleum hydrocarbon mixtures from his compressibility measurements, using the data on ethylene and isopentane to establish the curves for pure components. Kay also showed that for mixtures of the lower hydrocarbons whose composition was known the pseudocritical pressure and temperature could be calculated with fair accuracy from the critical pressures and temperatures of the pure components by the simple, or linear, mixture rule using mole fractions. In the case of complex hydrocarbon mixtures of unknown composition these methods may still be applied by making use of the "characterization factor" K, proposed by Watson and Nelson,[3] given by

$$K = \frac{(T_B)^{\frac{1}{3}}}{\text{Specific gravity}} \tag{V.124}$$

where T_B is the molal average boiling point in degrees Rankine, determined from a standard distillation, and the specific gravity is at $60°/60°F$. Kay[4] gives curves relating the pseudocritical pressures and temperatures to the molecular weight at constant values of K. Thus, knowing the average boiling point, specific gravity, and molecular weight of any petroleum hydrocarbon mixture, one can estimate, at least approximately, the volume at any pressure and temperature likely to be encountered in practice. More recently, Smith and Watson[5] have made a more exhaustive study of the critical properties of mixtures; they give a series of graphs from which both the true and pseudocritical pressures and temperatures of hydrocarbon mixtures can be estimated from A.P.I. gravity and certain average boiling points.

[1] THIELE, E. W., and W. B. KAY, *Ind. Eng. Chem.*, **25,** 894–898 (1933).

[2] KAY, W. B., *Ind. Eng. Chem.*, **28,** 1014–1019 (1936).

[3] WATSON, K. M., and E. F. NELSON, *Ind. Eng. Chem.*, **25,** 880–887 (1933).

[4] *Loc. cit.*

[5] SMITH. R. L., and K. M. WATSON, *Ind. Eng. Chem.*, **29,** 1408–1414 (1937).

For natural gases of unknown composition, the pseudocritical pressure and temperature can be related graphically to the specific gravity of the gas, as shown by Brown (see Illustration 7 for reference), and this gives a simple means of calculating the volume with fair accuracy.

Illustration 7.—A natural gas has the following composition:

Component	Mole Per Cent
CH_4	83.19
C_2H_6	8.48
C_3H_8	4.37
$i\text{-}C_4H_{10}$	0.76
$n\text{-}C_4H_{10}$	1.68
$i\text{-}C_5H_{12}$	0.57
$n\text{-}C_5H_{12}$	0.32
C_6H_{14}	0.63

Calculate the specific volume at 100°F. and 2,000 lb. per sq. in. abs.

The calculations of the average molecular weight, the pseudocritical temperature, and the pseudocritical pressure are indicated in the following tabulation:

(1) Component	(2) Mole fraction	(3) Molecular weight	(4) (2) × (3)	(5) Critical Temperature, °R.	(6) (2) × (5)	(7) Critical pressure, lb./sq. in. abs.	(8) (2) × (7)
CH_4	0.8319	16.04	13.31	344	286	673	560
C_2H_6	0.0848	30.07	2.54	549	46.5	712	60.4
C_3H_8	0.0437	44.09	1.92	666	29.1	617	27.0
$i\text{-}C_4H_{10}$	0.0076	58.12	0.44	732	5.56	544	4.13
$n\text{-}C_4H_{10}$	0.0168	58.12	0.97	766	12.86	551	9.26
$i\text{-}C_5H_{12}$	0.0057	72.15	0.41	829	4.72	483	2.75
$n\text{-}C_5H_{12}$	0.0032	72.15	0.23	846	2.71	485	1.55
C_6H_{14}	0.0063	86.17	0.54	914	5.75	435	2.74
			$\Sigma = 20.36$		$\Sigma = 393.2$		$\Sigma = 667.8$

$$T_R = \frac{100 + 460}{393.2} = 1.425$$

$$P_R = \frac{2000}{667.8} = 2.995$$

From Fig. V.2, $\qquad C = 0.765$

$$v = \frac{CRT}{pM} = \frac{0.765 \times 10.72 \times 560}{20.36 \times 2,000} = 0.113 \text{ cu. ft./lb.}$$

The experimental value of Sage and Lacey is 0.1064. Brown[1] solves this problem using a special compressibility-factor chart for natural gases and gets $v = 0.1066$ The ideal-gas volume would be 0.1479.

[1] BROWN, G. G., *Proc. 19th Annual Convention, Natural Gasoline Assoc. America,* May, 1940, pp. 54–74.

CHAPTER VI

THERMODYNAMIC PROPERTIES OF FLUIDS

General Discussion of Properties.—In studying various processes the engineer needs data on the thermodynamic properties of the fluids involved in the process, assembled in some form that is convenient for immediate use. In Chap. III we developed, in differential form, some of the fundamental relationships between the common thermodynamic properties—volume v (or the density ρ), energy E, enthalpy H, entropy S, work function A, free energy F, fugacity f, and activity a—and the state variables of pressure and temperature. In Chap. IV we extended these relationships for single-component single-phase systems to more complex systems, introducing the composition as a variable. In Chap. V we dealt at some length with one of the properties, *viz.*, the volume, and considered its variation with pressure, temperature, and composition and nature of the substance. In this chapter we shall show how some of the other properties are evaluated numerically by integration of the equations already derived and shall present some of the most commonly used methods of representing a network of some of the important thermo-dynamic properties of a given fluid in a convenient form for use. The engineer is more directly concerned with how to use these properties than with their evaluation; but to use them intelligently he should know something about the methods by which they are calculated, and it not infrequently happens that he is himself obliged to determine them.

The fluid under consideration may be a liquid at some pressure greater than the vapor pressure for the temperature in question (sometimes referred to as a "subcooled" liquid); a gas or vapor at a temperature above the temperature of saturation corresponding to the particular pressure (generally known as a "superheated" vapor); a saturated liquid or vapor (one at the saturation temperature or that temperature where the two phases are in equilibrium under the given pressure); or a mixture of saturated liquid and vapor (commonly known as "wet" vapor). Either the gas or liquid phase might consist of more than one component, but from considerations of space we shall restrict the treatment largely to cases of a single component or solutions of constant composition such as air.

The free energy F is mainly useful in the treatment of chemical equilibria. Since in this chapter we are concerned only with physical

changes, no further consideration will be given to F. The same applies to the function A.

It is well to call attention once more to the fact that volume, energy, enthalpy, and entropy are extensive properties; hence, their numerical values will depend on the mass of the system. In our treatment we shall deal almost entirely with specific (based on a unit mass) or molal (based on the molal mass as a unit) quantities.

There are certain properties not commonly represented in the usual tabulations of thermodynamic properties that, however, are of considerable importance. For example, the latent heat of vaporization of a liquid is a property of great utility, but it is really only a difference between two values of other properties, for example, either energy or enthalpy, depending on how one defines the latent heat. Other properties such as the specific heat at constant volume (C_v), the specific heat at constant pressure (C_p), and the Joule-Thomson coefficient ($\partial T/\partial p)_H$ are of importance for certain correlations and in the evaluation of other properties, as will be shown later.

It is, of course, desirable to obtain the complete network of properties from a minimum number of experimental measurements, and it is here that relationships such as those developed in Chap. III are of the greatest utility. Osborne and coworkers[1] at the Bureau of Standards have developed a method for determining the usual set of thermodynamic properties of fluids from direct determinations of enthalpy differences made in a single calorimetric setup, coupled with the vapor pressures. Keyes and coworkers[2] at the Massachusetts Institute of Technology have specialized on the measurement of volume and are able to derive most of the properties from volume data combined with vapor pressures and low-pressure specific heats.

Application of the Phase Rule.—Considering only a single-component system, the phase rule tells us that when only one phase is present there are two degrees of freedom, one degree of freedom when two phases coexist, and no degrees of freedom when three phases coexist. This means that when the fluid is entirely a liquid such as water or entirely a gas such as steam it is necessary to specify two independent variables before the state of the system is definitely fixed. For example, the tem-

[1] OSBORNE, N. S., *Bur. Standards J. Research*, **4**, 609–629 (1930). OSBORNE, N. S., H. F. STIMSON, and E. F. FIOCK, *Bur. Standards J. Research*, **5**, 411–480 (1930). FIOCK, E. F., *Bur. Standards J. Research*, **5**, 481–505 (1930). OSBORNE, N. S., H. F. STIMSON, and D. C. GINNINGS, *Mech. Eng.*, **57**, 162 (1935); *Bur. Standards J. Research*, **18**, 389–447 (1937).

[2] KEYES, F. G., L. B. SMITH, and H. T. GERRY, *Proc. Am. Acad. Arts Sci.*, **70**, 319–364 (1936). SMITH, L. B., F. G. KEYES, and H. T. GERRY, *Proc. Am. Acad. Arts Sci.*, **69**, 137–168 (1934). SMITH, L. B., and F. G. KEYES, *Proc. Am. Acad. Arts Sci.*, **69**, 285–314 (1934).

perature alone is not sufficient to define the volume or the enthalpy or any other property of steam; the pressure must also be given. When two phases are present—and these may be either a gas and a liquid, a liquid and a solid, or a gas and a solid—only one independent variable exists and the temperature alone (or the pressure) defines the system. Thus, when one has a mixture of steam and liquid water in equilibrium, the pressure and the thermodynamic properties of each phase are fixed once the temperature has been specified. They are entirely independent of the total volume of the system, which will vary with the relative amounts of the two phases present.

If three phases coexist, the system is nonvariant, which simply means that this situation can occur only at some one definite set of conditions and any change in pressure or temperature will cause the disappearance of one of the phases.
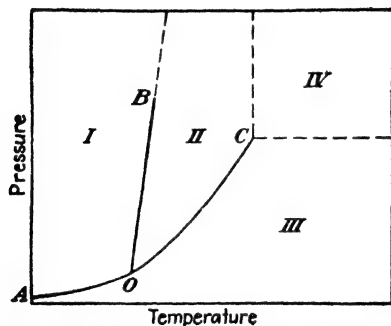
Fig. VI.1.—Simple phase diagram for a one-component system.

These very elementary facts, which should be clearly in mind before proceeding with a more detailed study of thermodynamic properties, are illustrated in Fig. VI.1. Field I is that where a solid phase is stable, II is the liquid region, and III is the gaseous region. It is clear that, in any of these areas, both pressure and temperature may be varied independently.

The boundary lines between the phases are the loci of points at which two phases can coexist. Thus OA is the so-called "sublimation curve" and represents equilibrium between the solid and vapor. OB is the melting or freezing curve, and along it a liquid and a solid are in equilibrium. Along OC liquid and vapor are in equilibrium. It is clear that along each line the pressure is definitely fixed by the temperature, or vice versa. Thus OC is the vapor-pressure curve of the liquid and OA that of the solid.

Curve OC is definitely terminated by the critical point C above the temperature of which no liquid can exist. Region II is therefore also bounded by a vertical line drawn from C (the critical isotherm) because no liquid can exist to the right of C. This is not, however, a definite boundary line in the same sense that OC is, because at temperatures above C it is possible to pass continuously from a gas to liquid, or vice versa, without any detectable discontinuity; but at temperatures below C it is necessary to cross the boundary line OC, and a visible separation into two phases of different density is observed.

By drawing the critical isobar also in Fig. VI.1, we establish a region IV the characteristic feature of which is that it is a region in which the vapor and liquid phases are indistinguishable. It is by traversing this region that one can bring about the change from a gas to a liquid without any discontinuity appearing. Since a substance in this region can be called neither a gas nor a liquid, we shall call it the "fluid" region for want of a better name. Region III will henceforth be called either the "gaseous" or the "superheated-vapor" region. The latter name is appropriate because of the fact that any gas in this region when cooled at constant pressure will reach the state of saturated vapor at which it will, upon further cooling, begin to deposit another phase, either liquid or solid. Note that this will not occur when a substance at a state in IV is cooled at constant pressure.

No limit has yet been found for curve OB. With a number of substances the pressure has been carried high enough so that the temperature is above that of point C, and the liquid changes to a gas. Thus we have a peculiar region in which the application of a high pressure to a gas can cause it to condense to a solid but never to a liquid. In a number of cases, there is a transition to another solid form, or there may be several such transition points; but in these cases the statement about the limit of curve OB is still valid if applied to the solid that is stable at the highest pressure.

The point O at which all three phases exist together is known as the "triple point." It is generally at a pressure of less than 1 atm., but there are some exceptions of interest. The most important from an industrial standpoint is carbon dioxide whose triple point is at $-56.6°C$. and 5.1 atm., or well above the normal boiling point of $-78.5°C$., which thus becomes a sublimation point.

Another exception to the general trends exhibited by Fig. VI.1 is that curve OB has a negative slope for some substances (notably water); in other words, increase in pressure lowers instead of raises the melting point. From the Clausius-Clapeyron equation in Chap. IV,

$$\frac{dp}{dT} = \frac{\Delta H}{T \, \Delta v} \qquad \text{(IV.153)}$$

it can be seen that this slope is related to the volume change which occurs when the substance melts. If there is an increase in volume (liquid less dense than solid), the slope will be positive; but if there is a contraction, as in the case of water, the slope will be negative.

In Fig. VI.1 only one solid phase is represented. Actually, many substances can have more than one solid phase, but this is seldom of any engineering significance. Thus, in the case of water, five other triple points besides the common one at $0.01°C$. and 0.00602 atm. are known,

involving several other solid forms; but the lowest one, in terms of pres-sure, occurs at about 2,000 atm.

Helium appears to be absolutely unique in two respects, (1) that it has two different liquid phases and (2) that it cannot be solidified at pressures of 1 atm. or lower at any temperature so far obtained. It has been solidified at higher pressures, and it appears that its melting curve (*OB* in Fig. VI.1) must intersect the pressure axis at a pressure above that corresponding to point *A* and hence no triple point exists.

THERMODYNAMIC DIAGRAMS AND TABLES OF PROPERTIES

General Types.—In the case of a pure fluid for which there are at the most only two independent variables, it is a relatively simple matter to represent most of the thermodynamic properties by means of a table or a graph using only two coordinates. A graph is particularly convenient and simple to use; the engineer who is dealing with the changes undergone by fluids in various processes has frequent use for such charts. Any chart that presents data on any of the properties listed at the beginning of this chapter will be known as a "thermodynamic diagram." The choice of coordinates is entirely arbitrary and is dictated largely by convenience, depending on the type of problem to be considered. Thus the following types of diagrams designated by the coordinates chosen have been commonly employed: temperature-entropy (*TS*); enthalpy-entropy (*HS*); enthalpy-pressure (*Hp*); and enthalpy-temperature (*HT*), or sensible heat, diagrams. Diagrams in which enthalpy is one of the coordinates, particularly the *HS* diagram, are commonly referred to as "Mollier diagrams." Diagrams in which the volume or a function of the volume such as the compressibility factor is one of the coordinates have been discussed in a previous chapter (page 156).

Many special diagrams may be desirable to aid in the solution of particular problems. For example, one may have occasion to plot C_p vs. T at various pressures or p vs. T at constant H (so-called "throttling curves") and many others.

When more than one component is present, the situation is much more complex. Even when we have only a binary system, there is a maximum of three degrees of freedom, and space diagrams with three coordinates would be necessary for complete representation. For more than two components, the complete portrayal of all the important properties is not feasible. In all cases of systems of more than one component, we are usually forced to consider at any one time only a restricted part of the whole field, *i.e.*, a restricted set of properties as compared with the range of properties that could be represented on a single diagram for a one-component system. Thus we might consider on one diagram certain properties at one given pressure or temperature and have separate

diagrams for other pressures or temperatures; or we might wish to consider a single composition and treat that just as one would a pure component (air is a case in point).

Outline of a Temperature-entropy Diagram.—Before plunging into a detailed consideration of various properties and the diagrams representing them, it will be helpful to consider one of the latter in general outline first. One of the most generally useful diagrams is the TS diagram, which is shown in outline form in Figs. VI.2 and VI.3. This particular form of the diagram is for a substance such as water or CO_2. Diagrams for other pure substances will be similar but will exhibit some important

Fig. VI.2.—Outline of a temperature-entropy diagram.

differences, one of which we shall mention later (page 254) when we consider specific heats of saturated vapors.

In Fig. VI.2, ACF is the boundary line between the single-phase regions II, III, and IV and the heterogeneous region VII where both liquid and vapor phases coexist. II is the liquid region corresponding to II in Fig. VI.1; likewise, III is the region of superheated vapor corresponding to III in Fig. VI.1, and IV is the region we have called the fluid region. Field I also corresponds to I in Fig. VI.1. Regions V, VI, and VII, in which two phases exist, appear merely as lines in Fig. VI.1, V corresponding to OB, VI to OA, and VII to OC. Point C, where a horizontal line is tangent to the boundary curve, is the critical point. Branch AC of the curve is known as the "saturated-liquid line" and CF as the "saturated-vapor line." ACG is the critical isobar,[1] branch CG

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[1] Because of the slight compressibility of a liquid, the isobars for moderate pressures in this region are only slightly separated, and hence for the purpose of this illustration they may be considered as identical with the saturated liquid line.

of which serves to make the arbitrary division between fields III and IV. The temperature corresponding to *BAF* is the triple-point temperature; and the region below it, bounded also by *BD* and *FH*, is the heterogeneous one in which solid and vapor are present. Note that there is no one point corresponding to the triple point in Fig. VI.1.

Referring now to Fig. VI.3, which represents (still in outline form but with greater detail than in the previous figure) a temperature-entropy
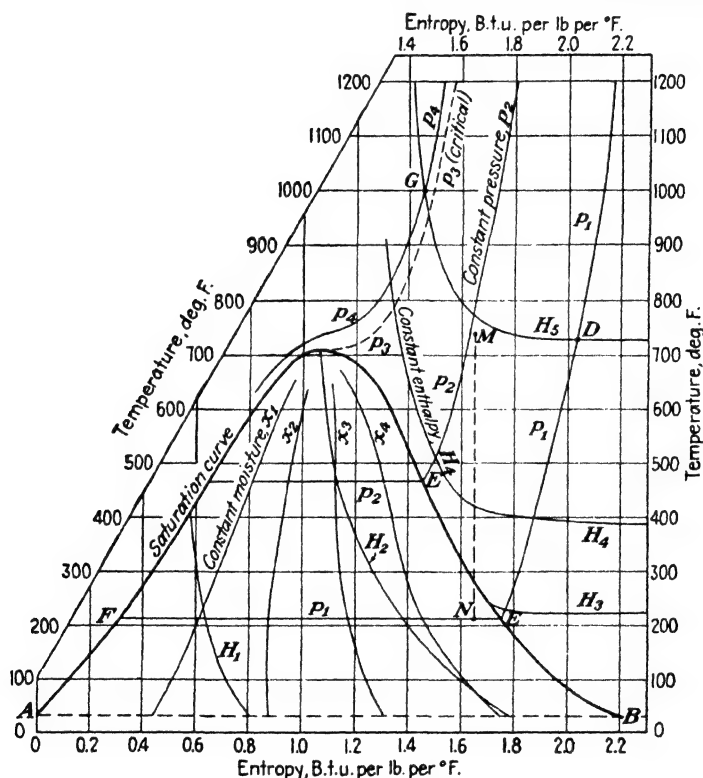
Fig. VI.3.—Outline of a temperature-entropy diagram for steam.

diagram for steam involving only the liquid and vapor phases, the lines marked p_1 to p_4 are lines along which the pressure is constant, or isobars, and lines H_1 to H_5 are lines of constant enthalpy, or isenthalps. By having a large number of these lines with equal increments of pressure and enthalpy between them, it is at once possible by interpolation to determine the entropy and the enthalpy of the fluid when its pressure and temperature are known or to determine its entropy and pressure when the other two are known, and similarly for other combinations.

On some diagrams, lines of constant superheat in degrees Fahrenheit are also shown. The superheat is the number of degrees that the actual temperature exceeds the saturation temperature for the given pressure. This is an important quantity since it gives one an immediate clue as to how closely a given vapor is approaching its condensation, or dew, point. The particular constant-pressure line that passes through the critical point C is, of course, the critical isobar, and the region lying above and to the right of the saturated-vapor line but below this isobar is the region of superheated vapor shown as III in Fig. VI.1. Thus, if we take any point in this region, such as D, the pressure is p_1 and the enthalpy H_5. Now, if one cools this vapor at constant pressure, this is equivalent to moving along the isobar p_1, and the change is continuous until one reaches the point E. At this point, the vapor becomes "saturated," and liquid begins to separate out as a second phase. This point is also known as the "dew point" though this term is more commonly used for the corresponding point in systems of more than one component.

As one continues to remove heat, the state of the system is represented by the horizontal line EF, since, there being now only one degree of freedom, an isobar is also an isotherm. As one removes heat in this region at constant pressure, the state of each phase remains constant and the only thing that changes is their relative amount. Thus, as we go from E to F, we pass in a continuous manner from a system that is 100 per cent vapor to one that is 100 per cent liquid. A point on the saturated-liquid line is also known as a "bubble point" from the fact that it represents an equilibrium between a relatively large amount of liquid and the last increment or bubble of vapor. (This term is more commonly used in the case of systems of more than one component.) In order quickly to determine the relative amounts of the two phases at any point in this region, there are drawn the lines x_1 to x_4 known as "constant-quality" or "constant-moisture lines." Any one of these lines connects all points for which the relative amounts of liquid and vapor are the same. A quality of 0.80 means that 1 lb. of total material contains 0.80 lb. of vapor and 0.20 lb. of liquid, and all points along the 0.80 quality line will represent mixtures of this same proportion. All the quality lines converge at the critical point where the two phases are identical.

Cooling of the saturated liquid at F along a constant-pressure line would involve passage along a curve that lies so close to the saturation line as to be practically indistinguishable from it on the scale of this diagram. Thus, at a given temperature, the entropy change with pressure is given by Eq. (III.94),

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \qquad \text{(III.94)}$$

and since the change of volume with temperature is quite small for liquids (except in the neighborhood of the critical point), the entropy does not change much with the pressure.   Therefore, for the majority of cases a constant-pressure line in the region of subcooled liquid (a liquid at a temperature lower than the boiling point) is substantially identical with the saturated-liquid line.

Fluid at a point such as G, which is at a pressure and temperature greater than the critical values, is in the region designated as IV in Fig. VI.1.   If the fluid in this state is cooled at constant pressure, it does not reach a saturation point where it deposits a second phase; instead, it passes by a series of continuous changes from a gaseous state to a liquid state, and it is impossible to choose any point at which it may be said to change abruptly, though the end points are quite different.   Thus the whole region above and to the left of the critical isobar is that peculiar one in which liquids gradually merge into gases, and vice versa.

The particular advantage of a diagram in which entropy is one of the coordinates lies in the fact that a reversible adiabatic-expansion or -compression process is one at constant entropy and such a process is very easy to trace on such a diagram, being merely a vertical line.   In Fig. VI.3, if the fluid is initially at the temperature and pressure represented by point M and it expands adiabatically (*i.e.*, without heat exchange with the surroundings) and reversibly (*i.e.*, ideally), the course of the changes through which it goes will be given by the vertical dotted line from M.   If the expansion is continued until the pressure drops to p_1, then N indicates the state of the fluid at the end of the expansion.   Its temperature, quality, and enthalpy are readily obtained from the chart.

Mollier Diagrams.—Another widely used chart is the enthalpy-entropy, or Mollier, chart, which is shown in outline in Fig. VI.4.   Not only has this chart the same advantage as the TS chart that a constant-entropy process is easy to follow, but also it is very convenient for getting accurate differences in enthalpy or for following a process at constant enthalpy.   Actually, of course, the same things can be obtained from either chart; it is wholly a matter of convenience which one is chosen.

The enthalpy-entropy diagram is but one of several types of chart proposed by Mollier[1] involving enthalpy as one of the coordinates.   The HS chart on ordinary rectangular coordinates is apt to be somewhat inconvenient in shape and particularly hard to read at the lower end. For this reason many prefer to adopt the suggestion of Mollier and use oblique coordinates.   Other Mollier charts that have been widely used are based on the following pairs of coordinates: Hv, H–$\log v$, Hp, and H–$\log p$.   The latter type has been particularly favored for work in

[1] MOLLIER, R., *Z. Ver. deut. Ing.*, **48**, 271–275 (1904).

refrigeration. Charts of this type for ammonia,[1] oxygen,[2] and nitrogen[2] are available in government publications.

Tables of Thermodynamic Properties.—For some applications it is more convenient to use tabulations of thermodynamic properties than a graph. The values of the properties can usually be obtained more
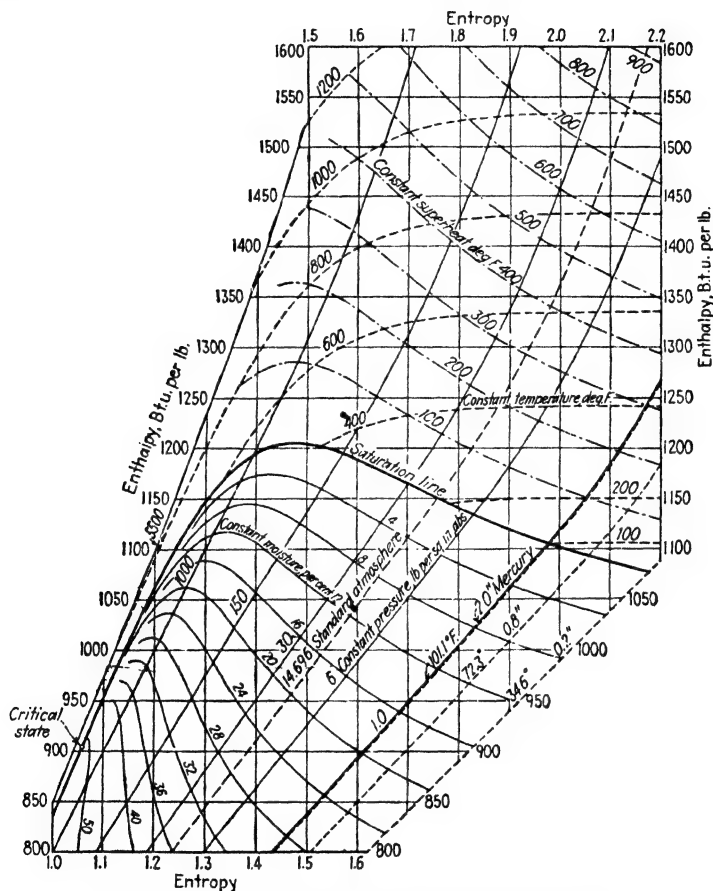
FIG. VI.4.—Outline of an enthalpy-entropy chart for steam.

accurately from the tables, and furthermore volumes are given in the tables but not usually on the diagrams because it complicates them too much and increases the difficulty of reading. Standard tables of thermo-

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[1] Tables of Thermodynamic Properties of Ammonia, *Bur. Standards Circ. No.* 142 (1923).

[2] MILLAR, R. W., and J. D. SULLIVAN, Thermodynamic Properties of Oxygen and Nitrogen, *Bur. Mines Tech. Paper* 424 (1928).

dynamic properties are available for a few of the most important fluids used industrially such as water, carbon dioxide, and ammonia. It is our intention in this section to give a brief description of such tables for the benefit of those who have not had occasion to use them before. As a specific example the Keenan-Keyes steam tables will be chosen.

The tables for a liquid-vapor system are generally divided into three sections as follows: Table 1, properties of saturated steam with temperature as the independent variable; Table 2, properties of saturated steam with pressure as the independent variable; Table 3, properties of superheated vapor.

In Table VI.1 a section of Table 1 of the Keenan-Keyes tables is reproduced:

TABLE VI.1.—PROPERTIES OF SATURATED STEAM WITH TEMPERATURE AS THE INDEPENDENT VARIABLE*

Temp. t, °F.	Abs. pressure p		Specific volume			Enthalpy			Entropy		
	lb./ sq. in.	In. Hg	Sat. liquid v'	Evap. Δv	Sat. vapor v''	Sat. liquid H'	Evap. ΔH	Sat. vapor H''	Sat. liquid S'	Evap. ΔS	Sat. vapor S''
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	·(12)
300	67.013	136.44	0.01745	6.449	6.466	269.59	910.1	1179.7	0.4369	1.1980	1.6350
302	69.046	140.58	0.01747	6.269	6.287	271.66	908.6	1180.3	0.4397	1.1929	1.6326
304	71.127	144.82	0.01749	6.096	6.114	273.72	907.2	1180.9	0.4424	1.1878	1.6302
306	73.259	149.16	0.01751	5.928	5.946	275.78	905.6	1181.4	0.4450	1.1828	1.6278
308	75.442	153.60	0.01753	5.766	5.783	277.85	904.1	1182.0	0.4477	1.1777	1.6254

* Reprinted by permission from "Thermodynamic Properties of Steam," by J. H. Keenan and F. G. Keyes, published by John Wiley & Sons, Inc.

The items tabulated in the various columns are as follows:

Column (1).—The temperature in degrees Fahrenheit. This covers the range from 32 to 705.4° (the critical point) in 1, 2, and 5° intervals, depending on the temperature.

Column (2).—The vapor pressure in pounds per square inch absolute at the temperature of column 1.

Column (3).—The same in inches of mercury.

Column (4).—The specific volume of the saturated liquid (*i.e.*, liquid under its vapor pressure) in cubic feet per pound.

Column (5).—The change in specific volume due to conversion of saturated liquid to saturated vapor at constant temperature, in cubic feet per pound.

Column (6).—Specific volume of saturated vapor in cubic feet per pound, or the sum of columns (4) and (5).

Column (7).—The enthalpy of saturated liquid in B.t.u. per pound based on a datum of zero for the enthalpy of saturated water at 32°F.

Column (8).—Enthalpy or latent heat of vaporization in B.t.u. per pound.

Column (9).—Enthalpy of saturated vapor, or column (7) plus (8).

Column (10).—Entropy of saturated liquid in B.t.u. per pound per degree Fahrenheit based on a datum of zero for the entropy of saturated water at 32°F.

Column (11).—Entropy of vaporization in same units.

Column (12).—Entropy of saturated vapor, or column (10) plus (11).

Values of the properties at other than the temperatures given can be obtained with sufficient accuracy by a linear interpolation.

In Table VI.2 a section of Table 2 of Keenan and Keyes is reproduced.

TABLE VI.2.—PROPERTIES OF SATURATED STEAM WITH PRESSURE AS THE INDEPENDENT VARIABLE*

Abs. press. p, lb./ sq. in.	Temp. t, °F.	Specific volume		Enthalpy			Entropy			Internal energy		
		Sat. liquid v'	Sat. vapor v''	Sat. liquid H'	Evap. ΔH	Sat. vapor H''	Sat. liquid S'	Evap. ΔS	Sat. vapor S''	Sat. liquid E'	Evap. ΔE	Sat. vapor E''
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
100	327.81	0.01774	4.432	298.40	888.8	1187.2	0.4740	1.1286	1.6026	298.08	807.1	1105.2
101	328.53	0.01775	4.391	299.15	888.2	1187.4	0.4750	1.1268	1.6018	298.82	806.5	1105.3
102	329.25	0.01775	4.350	299.90	887.6	1187.5	0.4759	1.1251	1.6010	299.57	805.9	1105.4
103	329.96	0.01776	4.310	300.64	887.1	1187.7	0.4768	1.1234	1.6002	300.30	805.3	1105.6
104	330.66	0.01777	4.271	301.37	886.5	1187.9	0.4778	1.1216	1.5994	301.03	804.7	1105.7

* Reprinted by permission from "Thermodynamic Properties of Steam" by J. H. Keenan and F. G. Keyes, published by John Wiley & Sons, Inc.

Column (1).—The vapor pressure in even values of pounds per square inch, from 0.20 to 3,206 lb. per sq. in. (the critical pressure). Below atmospheric pressure, the pressures are also given in inches of mercury down to 0.25 in.

Column (2).—The boiling point in degrees Fahrenheit corresponding to the pressure in column 1.

Columns (3) *to* (10).—The same data as in Table V.1 except that the volume change on evaporation has been omitted.

Columns (11), (12), *and* (13).—The energy in B.t.u. per pound of saturated liquid, energy of vaporization, and energy of saturated vapor, respectively. The energy was calculated from the values of H, p, and v by the equation

$$E = H - \frac{1}{J}(pv)$$

Table 3, an excerpt from which is given in Table VI.3, is very much larger than the other two because in the region of superheated vapor there are two independent variables instead of only one as was the case for the saturated region.

Column (1).—The pressure in pounds per square inch with the corresponding saturation temperature in degrees Fahrenheit in parentheses directly under it.

Column (3).—Volume v in cubic feet per pound, enthalpy H (h in the Keenan-Keyes tables) in B.t.u. per pound, and entropy S in B.t.u. per pound per degree Rankine, for saturated liquid.

Column (4).—The same for saturated vapor.

The quantities in these latter two columns are repeated from Table 2 for the sake of convenience in using Table 3 (Keenan and Keyes). The remaining columns in Table VI.3 give values of volume, enthalpy, and entropy corresponding to the temperature listed at the head of each column. Values are tabulated for pressures up to 5,500 lb. per sq. in. and temperatures to 1600°F.

EXAMPLES ILLUSTRATING USE OF THERMODYNAMIC DIAGRAMS AND TABLES

These will deal with simple changes of state, and all numerical values will be taken from the Keenan-Keyes steam tables or from the Mollier diagram accompanying these tables.

Illustration 1.—Water at 70°F. and atmospheric pressure (initial state, designated by subscript 1) is pumped into a boiler, evaporated at 300 lb. per sq. in. absolute pressure, and superheated to 600°F. at constant pressure (final state, subscript 2). How much heat must be supplied per pound of water?

Except for the step of pumping the water into the boiler, the whole process occurs at constant pressure; for such a process we have, by Eq. (III.10),

$$Q = \Delta H = H_2 - H_1$$

The effect of pressure on the enthalpy of a liquid is very small, and we may assume that the H of liquid water at 70°F. and the saturation pressure is the same as the H at 70°F. and 300 lb. per sq.in. From the tables,

$$H_2 = 1,314.7 \text{ B.t.u./lb.}$$
$$H_1 = 38.0 \text{ B.t.u./lb.}$$
$$\therefore Q = 1,276.7 \text{ B.t.u./lb. of water vaporized}$$

Illustration 2.—Saturated steam at 200 lb. absolute pressure expands continuously through a throttle to a constant pressure of 14.7 lb. per sq. in. What are the state of expanded steam and the entropy change in the process if no heat is lost to the surroundings (adiabatic process) and all kinetic energy due to any high-velocity jets is dissipated?

TABLE VI.3.—PROPERTIES OF SUPERHEATED STEAM*

Abs. press. lb./sq. in. (sat. temp.)	Property	Sat. liquid	Sat. vapor	Temperature, °F												
				320	330	340	350	360	370	380	390	400	420	440	460	480
84 (315.42)	v	0.018	5.226	5.265	5.349	5.433	5.515	5.597	5.677	5.757	5.836	5.915	6.071	6.225	6.377	6.529
	H	285.5	1184.0	1186.6	1192.3	1197.9	1203.5	1208.9	1214.3	1219.6	1224.8	1230.0	1240.0	1250.6	1260.7	1270.7
	S	0.4576	1.6168	1.6202	1.6274	1.6345	1.6413	1.6480	1.6545	1.6609	1.6671	1.6732	1.6851	1.6965	1.7076	1.7184
85 (316.25)	v	0.018	5.168	5.200	5.283	5.366	5.447	5.528	5.608	5.687	5.765	5.843	5.997	6.150	6.301	6.450
	H	286.4	1184.2	1186.4	1192.1	1197.7	1203.2	1208.7	1214.1	1219.4	1224.7	1229.9	1240.2	1250.4	1260.6	1270.6
	S	0.4587	1.6158	1.6186	1.6259	1.6330	1.6398	1.6465	1.6530	1.6594	1.6657	1.6718	1.6837	1.6951	1.7062	1.7171
86 (317.07)	v	0.018	5.111	5.136	5.219	5.300	5.381	5.461	5.540	5.618	5.696	5.773	5.925	6.076	6.225	6.374
	H	287.2	1184.4	1186.1	1191.9	1197.5	1203.0	1208.5	1213.9	1219.2	1224.5	1229.7	1240.1	1250.3	1260.4	1270.5
	S	0.4598	1.6149	1.6170	1.6243	1.6315	1.6383	1.6450	1.6516	1.6580	1.6642	1.6703	1.6823	1.6937	1.7049	1.7157

As will be shown in the next chapter, a throttling expansion is one at constant enthalpy. This gives the clue to find the final state of the steam, which is most readily accomplished with the use of the Mollier (*HS*) chart. Locate the point on the chart where the 200-lb. constant-pressure line crosses the saturation line. This is the initial state, and from the coordinates of the chart we obtain the values

$$H_1 = 1,198.4, \qquad S_1 = 1.545$$

Now proceed horizontally on the chart (constant *H*) to the intersection with the 14.7-lb. constant-pressure line; this is the final state. Read the values.

$$S_2 = 1.823$$
$$t_2 = 311.5°F.$$
$$\Delta S = 1.823 - 1.545 = 0.278$$
$$\text{Degrees of superheat} = 99°F.$$

The two temperatures are estimated by interpolation between the lines of constant temperature and lines of constant superheat, respectively.

The same problem can be solved almost as readily by the tables.[1] Locate the initial point in Table 2; then go to Table 3 and proceed horizontally from $p = 14.7$ to the enthalpies nearest the known value of 1,198.4. By linear interpolation between the two *H* values on either side of the given one, the final *t* and *S* are obtained. From the tables we may also obtain the volumes, none of which is given on the chart.

Illustration 3.—Superheated steam at 200 lb. per sq. in. absolute pressure and with 50°F. of superheat expands adiabatically and reversibly to a final pressure of 14.7 lb. abs. Give the final state and the change in *H*.

A reversible adiabatic change is one at constant entropy. Locate the initial point as before, interpolating between the lines of constant superheat.

$$S_1 = 1.582$$
$$H_1 = 1,230$$

Drop vertically along a constant *S* line to the intersection with the standard atmospheric-pressure line. The final state is in the two-phase region. It is a mixture of steam and droplets of liquid water, the latter being 12.1 per cent by weight of the total, or the quality is 0.879. $H_2 = 1,032$, and $\Delta H = -198.5$.

This problem is also readily solved from the tables by imposing the condition

$$S_2 = S_1 = 1.582$$

where each *S* refers to 1 lb. of the total material at the given state. The problem then is to find a final state whose pressure is 14.7 lb. and whose entropy is 1.582. Reference to Table 3 (in Keenan and Keyes) shows at a glance that all the entropies at this pressure are higher than 1.582 and therefore we conclude that the final state of the steam is not in the superheated region but must be in the two-phase region. Consequently, we can write

$$S_2 = S_2' + x_2 \Delta S \qquad [\text{see Eq. (VI.54)}]$$

where $S_2' = $ entropy of the liquid.

$\Delta S = $ entropy change due to vaporization.

$x_2 = $ quality.

Since the state is in the two-phase region, we are dealing with a mixture of saturated liquid and saturated vapor at 14.7 lb. pressure, and the following values are obtained at once from the tables:

[1] Reference here is to the complete Keenan-Keyes tables, *op. cit.*

$$S_2' = 0.3120$$
$$\Delta S = 1.4446$$
$$\therefore 1.582 = 0.3120 + 1.4446x$$
$$x = 0.879$$

and also

$$H_2 = H_2' + x_2\,\Delta H$$
$$= 180.1 + 0.879 \times 970.3 = 1{,}033$$
$$v_2 = v_2' + x_2\,\Delta v$$
$$= 0.017 + 0.879 \times 26.78 = 23.54 \text{ cu. ft./lb. of mixture}$$

CALCULATION OF PROPERTIES IN THE SUPERHEATED REGION

Having considered a general outline of the thermodynamic network of properties, we shall now consider in more detail some of the methods for the calculation of particular properties. In this section the emphasis will be on the superheated-vapor region (III in Fig. VI.1), but it should be understood that the relationships apply equally well to any single-phase region, for example, to the liquid region (II in Fig. VI.1) and to the fluid region (IV in Fig. VI.1).

Analytical Methods.—The equations of Chap. III plus a suitable equation of state provide one method for the calculation of the thermodynamic properties of pure substances in the superheated region. This is probably the simplest method if the constants of the equation of state are known, but it must be recognized that it is likely to be only an approximate method even with the best equations of state.

For the calculation of E, an equation of state explicit in p is most directly useful; for H, the equation explicit in v is the simplest. For calculation of S it makes little difference which type of equation is used. Equations explicit in p are much the commoner of the two, and by a simple transformation to be illustrated below they can readily be used to calculate enthalpies.

Robinson and Bliss[1] give the complete analytical expressions for calculation of isothermal changes in E, H, and S from three equations of state explicit in p, *viz.*, van der Waals', Wohl's, and Beattie-Bridgeman's. Comparison of the calculated values for three different gases with values calculated from pvT data by graphical means revealed that the Beattie-Bridgeman equation was superior to the other two, especially for the calculation of enthalpy. Even with this equation, deviations were as much as 7 per cent for entropy and 12 per cent (or more in a few cases) for enthalpy.

Enthalpy.—Qualitatively, enthalpy generally increases with the temperature and decreases with pressure increase. These are good rules for general guidance though there are exceptions in a few cases.

[1] ROBINSON, H. M., and H. BLISS, *Ind. Eng. Chem.*, **32**, 396–398 (1940).

In this region, enthalpy is generally calculated from measurements of other properties though the value on the saturation line is often obtained from calorimetric measurements of the latent heat of vaporization. Recently extensive direct measurements of the enthalpy of steam throughout the superheated region have been made.[1] The principle of such measurements is very simple. Steam at the desired initial pressure and temperature is continuously expanded to atmospheric pressure through a throttle and then completely condensed in a calorimeter condenser. The heat given out is measured by the rise in temperature of cooling water. After correcting for heat losses, the heat gained by the cooling water is equal to the difference in H between the initial high-pressure steam and the condensate. The amount of steam is determined by weighing the condensate.

The fundamental equation for calculation of the enthalpy of any homogeneous substance when the independent variables are p and T is Eq. (III.96), *viz.*,

$$dH = C_p \, dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp \qquad \text{(III.96)}$$

Integration gives

$$H = H_0 + \int_{T_0}^{T} C_p \, dT + \int_{p_0}^{p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp \qquad \text{(VI.1)}$$

where H_0 is an initial, arbitrary value of H at some initial value of p and T. The common practice is to let $H = 0$ for the saturated liquid at the ice point (32°F.). H_0 in this equation will then be simply the difference in enthalpy between the vapor at p_0 and T_0 and the saturated liquid at the ice point. If p_0 is the vapor pressure at T_0 and T_0 is at the ice point, then H_0 equals the latent heat of vaporization at the ice point.

As explained in Chap. I, this equation may be integrated in two ways. Since specific-heat data are seldom available at any high pressures, it is clear that the proper procedure in this case is to integrate first with respect to temperature variation. The use of this equation will be illustrated by the following example.

Illustration 4.—Calculate the enthalpy of nitrogen at $-100°C$. and 50 atm. absolute pressure.

Since the value of H_0 in Eq. (VI.1) is entirely arbitrary, it could be taken equal to zero or to any value desired; but in order to compare our calculated result with that obtained from an existing compilation of the thermodynamic properties of nitrogen, we shall let $H_0 = 2,696$ c.h.u. per lb.-mole[2] when $T_0 = 273.2°K$. and $p_0 = 1$ atm. One needs to know C_p as a function of temperature at low pressure in order to evaluate

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[1] HAVLIČEK, J., and L. MIŠKOVSKÝ, *Helvetica Phys. Acta*, **9**, 161–207 (1936).
[2] Value from Table 6, Millar and Sullivan, *op. cit.*

the first integral. Brinkworth[1] gives the following equation for molal heat capacity of nitrogen at 1 atm. and at temperatures below 0°C.:

$$C_p = 7.40 - 0.00405T + 8.272 \times 10^{-6}T^2$$

Utilizing this equation to evaluate the first integral in Eq. (VI.1),

$$\int_{T_0}^{T} C_p \, dT = \int_{T_0}^{T} (7.40 - 0.00405T + 8.272 \times 10^{-6}T^2) \, dT$$

$$= 7.40(T - T_0) - \frac{0.00405}{2}(T^2 - T_0^2) + \frac{8.272 \times 10^{-6}}{3}(T^3 - T_0^3)$$

Substituting $T = 173.2$ and $T_0 = 273.2$, the value of the integral is -692.

Evaluation of the second integral requires a knowledge of the pvT behavior of nitrogen over the range in question. If a series of tabulated values of the volume and the coefficient $(\partial v/\partial T)_p$ is available, the integration could be performed graphically. This would require a knowledge of v as a function of p at the temperature T (173.2°K. in this case) and also v as a function of T over the pressure range in question in order to obtain the coefficient $(\partial v/\partial T)_p$. [The graphical evaluation of thermodynamic properties will be further illustrated in a later section of this chapter (page 234).]

The simplest way to evaluate the second integral is by means of an equation of state. This is an accurate means provided that the equation used is known to hold accurately over the range in question. The simple equation of state: $pv = RT$ gives

$$\int_{p_0}^{p} RT \frac{dp}{p} - \int_{p_0}^{p} RT \frac{dp}{p} = 0$$

a result we could have anticipated from one of the definitions of the ideal gas, *viz.*, that its energy, and hence its enthalpy, is independent of the pressure.

The Beattie-Bridgeman equation of state has been shown to be quite accurate, and the constants for N_2 are known. To evaluate $\int v \, dp$ it is convenient to have an equation of state that gives v explicitly. Beattie rearranged the equation of state to give one in this form [Eq. (V.84)], but it is less reliable than the original explicit-pressure form, and therefore for this problem let us assume that the original form [Eq. (V.77)] is to be used. One way to proceed is to transform $\int v \, dp$ as follows:[2]

$$d(pv) = p \, dv + v \, dp \tag{1}$$

$$\int_{p_0}^{p} v \, dp = pv - p_0 v_0 - \int_{v_0}^{v} p \, dv \tag{2}$$

Furthermore, the coefficient $(\partial v/\partial T)_p$ is not convenient to work with in the case of an equation not explicit in the volume, and it may be transformed as follows:

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial p}\right)_T$$

At constant T,
$$\left(\frac{\partial v}{\partial T}\right)_p dp = -\left(\frac{\partial p}{\partial T}\right)_v dv \tag{3}$$

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[1] BRINKWORTH, J. H., *Proc. Roy. Soc.*, **A3**, 124–133 (1926).

[2] An alternative to the method given here is to use the coefficient $(\partial H/\partial v)_T$, which is related to the state variables as follows:

$$\left(\frac{\partial H}{\partial v}\right)_T = v\left(\frac{\partial p}{\partial v}\right)_T + T\left(\frac{\partial p}{\partial T}\right)_v$$

This is readily evaluated by an equation of state explicit in p.

Using Eqs. (2) and (3),

$$\int_{p_0}^{p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp = pv - p_0 v_0 - \int_{v_0}^{v} p \, dv + T \int_{v_0}^{v} \left(\frac{\partial p}{\partial T} \right)_v dv \qquad (4)$$

By differentiation of the Beattie-Bridgeman equation (V.77),

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v} + \frac{\alpha_0}{v^2} + \frac{\beta_0}{v^3} - \frac{\gamma_0}{v^4} \qquad (5)$$

where

$$\alpha_0 = RB_0 + \frac{2Rc}{T^3}$$

$$\beta_0 = \frac{2RcB_0}{T^3} - RB_0 b$$

$$\gamma_0 = \frac{2RcbB_0}{T^3}$$

Using the equation of state in the form of Eq. (V.78),

$$\int p \, dv = RT \int \frac{dv}{v} + \beta \int \frac{dv}{v^2} + \gamma \int \frac{dv}{v^3} + \delta \int \frac{dv}{v^4} \qquad (6)$$

β, γ, and δ are temperature functions whose definitions are given on page 183.

$$\int_{v_0}^{v} p \, dv = \left[RT \ln v - \frac{\beta}{v} - \frac{\gamma}{2v^2} - \frac{\delta}{3v^3} \right]_{v_0}^{v} \qquad (7)$$

From Eq. (5),

$$T \int_{v_0}^{v} \left(\frac{\partial p}{\partial T} \right)_v dv = \left[RT \ln v - \frac{\alpha_0 T}{v^2} - \frac{\beta_0 T}{2v^2} - \frac{\gamma_0 T}{3v^3} \right]_{v_0}^{v} \qquad (8)$$

Substituting Eqs. (7) and (8) in Eq. (4),

$$\int_{p_0}^{p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp = pv - p_0 v_0 - \left[\alpha_1 \left(\frac{1}{v} - \frac{1}{v_0} \right) + \beta_1 \left(\frac{1}{v^2} - \frac{1}{v_0^2} \right) - \gamma_1 \left(\frac{1}{v^3} - \frac{1}{v_0^3} \right) \right] \qquad (9)$$

where

$$\alpha_1 = A_0 + \frac{3Rc}{T^2}$$

$$\beta_1 = \frac{3RcB_0}{2T^2} - \frac{aA_0}{2}$$

$$\gamma_1 = \frac{RB_0 bc}{T^2}$$

v must be obtained from the equation of state by a trial process. For this specific problem it is the volume at $T = 173.2$ and $p = 50$, and the final trial value obtained by using the constants given in Table V.4 is 0.233 liter per gram-mole. v_0 can be obtained with sufficient accuracy from the ideal-gas law.

$$v_0 = \frac{RT}{p_0} = \frac{0.08206 \times 173.1}{1} = 14.21 \text{ liters/g.-mole}$$

$$\alpha_1 = 1.690, \qquad \beta_1 = -0.00892, \qquad \gamma_1 = -0.0000400$$

Substitution of these values in Eq. (9) gives, for the numerical value of the second integral. -9.53. This is in mechanical units of liter-atmospheres per gram-mole and

must be converted to gram-calories to put it on the same basis as the other terms in Eq. (VI.1).

$$-9.53 \times 24.20 = -231 \text{ g.-cal.}$$

Finally, H at $-100°C.$ and 50 atm. $= 2,696 - 692 - 231 = 1,773$ c.h.u. per lb.-mole. (For comparison, the value obtained by interpolation in Table 6, Millar and Sullivan, *op. cit.*, is 1,780.)

Another method of solving this problem is to obtain ΔE by using Eq. (III.79) and then calculate ΔH from

$$\Delta H = \Delta E + \Delta(pv)$$

This method is really the same as the one just followed since it involves the same integrals.

Energy Content.—This is of much less importance from a practical standpoint than the enthalpy, and values are seldom given in compilations of thermodynamic properties. On the other hand, it is required in certain problems, and the simplest way to obtain it is from the enthalpy by the equation

$$E = H - pv$$

Illustration 5.—What is the energy content of superheated steam at 200 lb. per sq. in. abs. and 600°F.?

From the Keenan-Keyes steam tables we have

$$H = 1,322.1 \text{ B.t.u./lb.}$$
$$v = 3.060 \text{ cu. ft./lb.}$$

Then, $E = 1,322.1 - \dfrac{200 \times 144 \times 3.060}{778.3} = 1,209.0$ B.t.u./lb. (778.3 is the mechanical equivalent of heat in foot-pounds per B.t.u.).

Illustration 6.—A closed vessel of 10.0 cu. ft. volume is filled with saturated steam at 265 lb. per sq. in. abs. If 25 per cent of the steam is then condensed, what would be the pressure in the vessel and how much heat must be removed to cause the condensation?

$$v_1 = 1.742 \text{ cu. ft./lb.} \qquad \text{(from the steam tables)}$$
$$\text{Lb. of steam} = \frac{10.0}{1.742} = 5.74$$

After condensation there is $0.75 \times 5.74 = 4.30$ lb. of steam left. Neglecting the volume of the liquid, v_2, the final specific volume $= 10.0/4.30 = 2.325$. From the tables, $p_2 = 196.7$ lb. per sq. in. abs. Since this is a constant-volume process, the heat effect Q is given by ΔE and not by ΔH.

$E_1 = 1,116.3$ $\bigg[$ read directly from table. When not tabulated, it can be calculated

from $E = H - (pv)\dfrac{1}{J}\bigg]$

$$E_2 = E \text{ of liquid } +0.75 \, \Delta E \text{ of vaporization}$$
$$= 353.2 + 0.75(760.3) = 923.2$$
$$\Delta E \text{ (per lb.)} = 1,116.3 - 923.2 = 193.1 \text{ B.t.u.}$$
$$\therefore Q = 5.74 \times 193.1 = 1,110 \text{ B.t.u.}$$

Effect of Pressure on Specific Heat.[1]—In dealing with the transfer of heat to and from fluids under pressure, the engineer generally makes use of values of enthalpy and does not have to consider the specific heat. There are circumstances, however, in which it is convenient to use data on the specific heat of fluids under pressure to calculate heat effects; furthermore, this property is frequently useful in various correlations and as a means of checking other thermodynamic properties. Very few direct measurements of the specific heat of fluids at elevated pressures have been made, and consequently it is desirable to consider briefly the ways in which the change in specific heat with pressure can be calculated. The following exact equations form the basis for calculation of the effect of pressure on specific heats:

$$C_p = C_{p^\circ} - \frac{T}{J} \int_{p^\circ}^{p} \left(\frac{\partial^2 v}{\partial T^2} \right)_p dp \tag{VI.2}$$

$$C_v = C_{v^\infty} + \frac{T}{J} \int_{v^\infty}^{v} \left(\frac{\partial^2 p}{\partial T^2} \right)_v dv \tag{VI.3}$$

$$C_p - C_v = \frac{T}{J} \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p \tag{III.112}$$

p° (or v^∞) refers to a state at some convenient low pressure, usually 1 atm., below which the specific heat is, for all practical purposes, independent of pressure. Equations (VI.2) and (VI.3) result directly from the integration of Eqs. (III.105) and (III.104), the mechanical equivalent J being added so that it will not be overlooked in a numerical calculation.

For the special case of an ideal gas we have already seen that

$$\left(\frac{\partial C_v}{\partial v} \right)_T = 0 \tag{III.157}$$

and

$$\left(\frac{\partial C_p}{\partial p} \right)_T = 0 \tag{III.158}$$

In other words, for the ideal gas, the specific heats at constant volume and at constant pressure do not change with the pressure (or the volume), and therefore the effect of pressure on the specific heat of real gases is closely related to the question of their deviations from the law of ideal gases. This is a useful qualitative result because it tells us at once that for most calculations we can ignore the effect of pressure on specific heat since it becomes significant only when the deviations from the ideal state are large.

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[1] The term "specific heat" is commonly used rather loosely to include molal heat capacity as well as true specific heat. We shall continue this practice and not distinguish between them except when giving numerical values.

Furthermore, for the ideal gas, or approximately for any gas at low pressure,

$$C_p - C_v = R \qquad \text{(III.159)}$$

The following qualitative statements about the effect of pressure on specific heat are useful: The percentage increase in C_p over the value at 1 atm. may easily be as much as 25 per cent for gases well above their critical temperature and at pressures of 1,000 atm. The higher the temperature, the less the effect; and near the critical temperature the increase becomes very great as it must since $C_p = \infty$ at the critical temperature. The effect of pressure on C_v is very much less, as is evident from Eq. (VI.3) and the fact that the isometrics of gases are very nearly linear except at very high densities.

From Eq. (VI.2) it is evident that C_p at high pressure can readily be calculated if the pvT data for the gas in question and its C_p at low pressure are known. The actual calculation can be made graphically or algebraically, the latter method being the simpler if an equation of state is already available. In either case, very accurate compressibility data or an accurate equation of state must be available to obtain reliable values of C_p because of the second derivative.

Illustration 7.—Calculate the specific heat at constant pressure of a naphtha vapor at $600°$F. and 300 lb. per sq. in. absolute pressure, given the following data:

1. The constants of a Linde equation of state [Eq. (V.68)] for the vapor are

$$A = 157 \qquad C = 7,234 \times 10^7 \qquad D = 20 \qquad E = 102 \times 10^7 \qquad F = 0.52$$

for p in pounds per square inch, v in cubic inches per pound; and T in degrees Rankine.

2. The specific heat of the vapor at 1 atm. is given by the equation

$$C_p = 0.000504(t + 670)$$

where C_p is in B.t.u. per pound per degree Fahrenheit and t in degrees Fahrenheit. By differentiation of the equation of state,

$$-T \left(\frac{\partial^2 v}{\partial T^2}\right)_p = \frac{12(C - Ep)}{T^4}$$

From Eq. (VI.2),

$$C_p = C_{p_1} + \frac{12J}{T^4} \int_{p_1}^{p} (C + Ep)\,dp$$

$$= C_{p_1} + \frac{12CJ}{T^4}(p - p_1) + \frac{6EJ}{T^4}(p^2 - p_1^2)$$

$$C_{p_1} = 0.000504(600 + 670) = 0.640$$

$$J = 778 \times 12$$

Substituting values,

$$C_p = 0.640 + 0.0675 = 0.708$$

The derivative $(\partial^2 v / \partial T^2)$ may be quite involved and cumbersome to handle for an equation of state explicit in p, and for this case it is simpler to calculate C_p by a combination of Eqs. (VI.3) and (III.112).

Illustration 8.—Calculate the specific heat C_p of air at 0°C. and 200 atm., given the constants of the Keyes equation of state and that C_p at 1 atm. $= 0.240$ B.t.u. per lb. per °F.

The Keyes equation of state is

$$p = \frac{2.833T}{v - \delta} - \frac{A}{(v - l)^2} \tag{V.70}$$

where $\delta = \beta e^{-\frac{\alpha}{v}}$.

For air,

$$\alpha = 0.682, \qquad \beta = 1.589$$
$$A = 1{,}605.3, \qquad l = -0.088$$

when p is in atmospheres, v in cubic centimeters per gram, and T in degrees Kelvin. By differentiation of the equation of state,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - \delta}$$

and

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0$$

Therefore, by Eq. (VI.3), C_v is independent of pressure.

By differentiation of the equation of state,

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{v - \delta}{T} \frac{1}{1 - \frac{\alpha\delta}{v^2} - \frac{2A}{RT}\frac{(v - \delta)^2}{(v - l)^3}} \tag{1}$$

and

$$T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{1 - \frac{\alpha\delta}{v^2} - \frac{2A}{RT}\frac{(v - \delta)^2}{(v - l)^3}} = J(C_p - C_v) \tag{2}$$

Since at low pressure the terms involving v are only small correction terms, it is sufficiently accurate to use the ideal volume.

$$v_{\text{ideal}} = \frac{82.06 \times 273}{29.0} = 773 \text{ cc./g.}$$

For this particular case, (2) can be simplified to

$$J(C_p - C_v) = \frac{R}{1 - (2A/RTv)}$$
$$= 2.845 \text{ cc.-atm./g.}$$
$$C_p - C_v = 2.845 \times 0.02422 = 0.0683 \text{ g.-cal./g.}$$
$$\therefore C_v = 0.240 - 0.068 = 0.172 \qquad \text{(at 1 atm.)}$$

Since C_v is independent of the pressure, this is also the value at 200 atm.

By trial solution of the Keyes equation, v at 200 atm. and 0°C. $= 3.900$ cc. per g. Again utilizing (2),

$$C_p - C_v = \frac{2.833}{(1 - 0.0599 - 0.431)J} = 0.1350$$
$$\therefore C_p = 0.172 + 0.135 = 0.307$$

Relatively simple expressions for specific heat as a function of pressure may be obtained by dropping certain terms from the equations

that result when the differential equations such as Eq. (VI.2) are integrated with the aid of equations of state. Thus Beattie[1] obtained the following equation by using this procedure in conjunction with the Beattie-Bridgeman equation of state:

$$C_p = C_{p^\circ} + \left(\frac{2A_0}{RT^2} + \frac{12c}{T^4} \right) p \qquad (VI.4)$$

where A_0 and c are the equation-of-state constants. This, of course, is only an approximation, but it appears to give good results as long as pressures are not too high and the temperature is well above the critical.
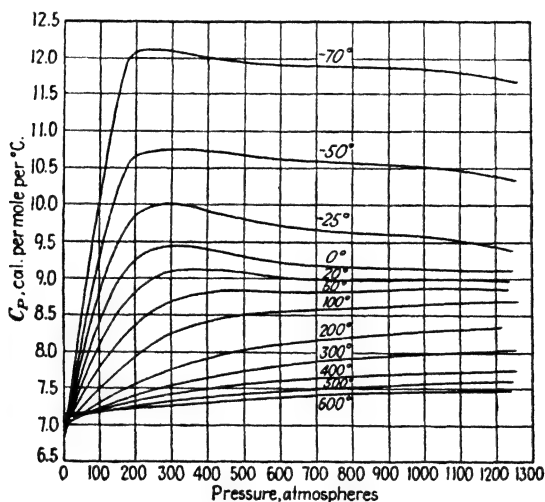
FIG. VI.5.—Effect of pressure on the specific heat of nitrogen. [*Data of Deming and Shupe, Phys. Rev.,* **37,** 638-654 (1931).]

Deming and Shupe have calculated the effect of pressure on the specific heat of hydrogen,[2] nitrogen,[3] and carbon monoxide[4] by means of Eq. (VI.2), using graphical methods to evaluate the second derivative and the integral. Their values for nitrogen shown in Fig. VI.5 serve to give a general idea of the way in which pressure affects C_p in the case of a substance that is highly superheated, *i.e.*, far removed from the state of a saturated vapor. Mackey and Krase[5] have measured C_p of nitrogen at pressures up to 800 atm. for several temperatures, and the agreement

[1] BEATTIE, J. A., *Phys. Rev.,* **34,** 1615–1620 (1929).
[2] DEMING, W. E., and L. E. SHUPE, *Phys. Rev.,* **40,** 848–859 (1932).
[3] DEMING, W. E., and L. E. SHUPE, *Phys. Rev.,* **37,** 638–654 (1931).
[4] DEMING, W. E., and L. E. SHUPE, *Phys. Rev.,* **38,** 2245–2264 (1931).
[5] MACKEY, B. H., and N. W. KRASE, *Ind. Eng. Chem.,* **22,** 1060 (1930).

between the calculated and experimental values is probably within the accuracy of the experimental measurements. A recent publication[1] gives the results of calculations of the effect of pressure on C_p for eight gases by means of the Beattie-Bridgeman equation of state.
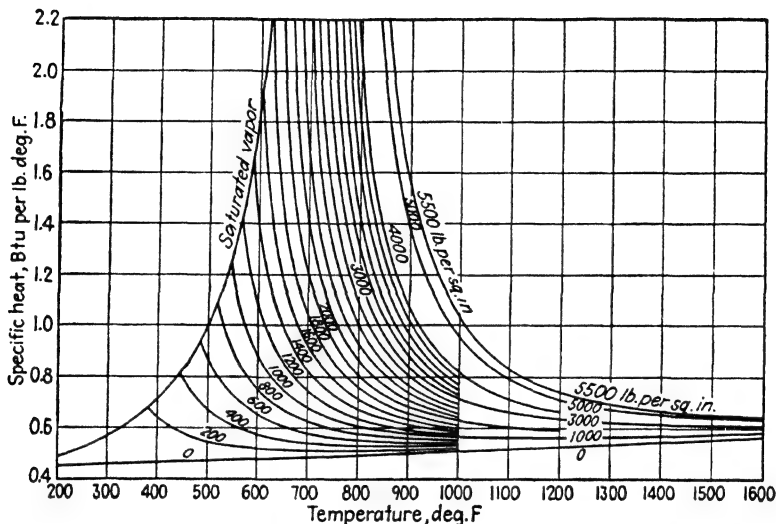
FIG. VI.6.—Constant-pressure specific heat of water vapor at high pressure. (*Reprinted by permission from "Thermodynamic Properties of Steam" by J. P. Keenan and F. G. Keyes, published by John Wiley & Sons, Inc.*)

Values of the specific heat at constant pressure can be readily calculated from enthalpy values by the equation

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

Since there is available a wealth of accurate enthalpy data for steam, a rather complete picture of the effect of pressure on C_p of a saturated and slightly superheated vapor is obtained from these data. Figures VI.6 and VI.7 give C_p for water vapor as a function of pressure and temperature. Figure VI.6 is incomplete in that it does not show both branches of the isobars for the pressures above critical, and hence Fig. VI.7 is added to show more completely the behavior at high pressures. Some very interesting and striking facts are shown by these figures. For example, one is accustomed to thinking of C_p as always increasing with the temperature; but these figures show that, at elevated pressures below critical, C_p decreases with increase in temperature until very high

[1] ELLENWOOD. F. O., N. KULIK, and N. R. GAY, *Cornell Univ. Eng. Expt. Sta Bull.* **30** (1942).

temperatures are reached. The rapidity of the change with temperature in the neighborhood of the saturation line is also noteworthy. Below the critical point the specific heat increases very rapidly as one approaches
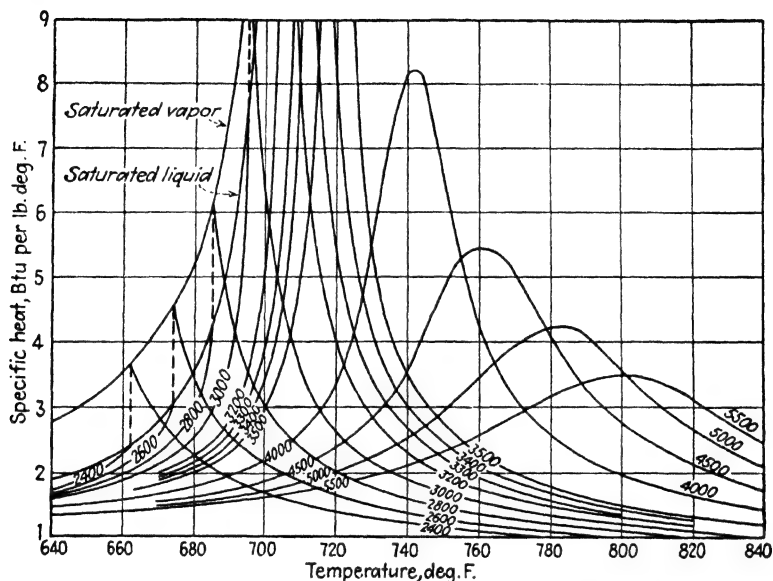
Fig. VI.7.—Constant-pressure specific heat of water vapor in the region near the critical point. (*Reprinted by permission from "Thermodynamic Properties of Steam" by J. P. Keenan and F. G. Keyes, published by John Wiley & Sons, Inc.*)

this point and becomes infinite at the critical point itself, as would be expected from the following considerations:

By Eq. III.109,
$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{(\partial p/\partial T)_v}{(\partial v/\partial T)_p}$$

From the behavior of gases discussed in Chap. V, it is evident that $(\partial p/\partial T)_v$ is a finite quantity at the critical point. By Eq. (V.38),

$$\left(\frac{\partial p}{\partial v}\right)_{T_c} = 0$$

$$\therefore \left(\frac{\partial v}{\partial T}\right)_p = \infty$$

Finally, by Eq. (III.112), $\quad C_p = \infty$

Above the critical pressure (3,200 lb. per sq. in.) the C_p vs. temperature curve rises rapidly to a maximum and then decreases, the maximum becoming less sharp as the pressure increases.

Another important application of Eqs. (VI.2) and (VI.3) is in checking the consistency of thermodynamic-property data. If one has a set of volume measurements on some substance and, from another source, a set of C_p values, the two can be compared by means of these equations. This furnishes a very sensitive test of the accuracy of the volume data.

Derivation of Volume from C_p.—The fact that specific-heat data can be used to obtain specific volumes is not generally appreciated. This is not only an interesting application of thermodynamics but one of practical importance as well. A German steam table[1] was based on just such a calculation. If Eq. (III.105) is integrated twice, we get

$$v = \phi(p) + T\psi(p) - \int \int \frac{1}{T} \frac{\partial C_p}{\partial p} \, dT \, dT \qquad \text{(VI.5)}$$

where $\phi(p)$ and $\psi(p)$ are functions of p only. If the gas can be assumed ideal at some initial high temperature, then $\partial C_p/\partial p = 0$ and

$$\phi(p) + T\psi(p) = \frac{RT}{p}.$$

The available data indicate that such a limiting assumption is not a good one. We do know, however, that $pv = RT$ as $p \to 0$, at any temperature, and this condition is satisfied if one writes

$$\psi(p) = \frac{R}{p} + \psi_1(p)$$

and if $\psi_1(p)$ and $\phi(p)$ remain finite as $p \to 0$. These functions must be evaluated from experimental data.[2] The combined terms $\phi(p) + T\psi(p)$ of Eq. (VI.5) are simply equal to the volume at the initial temperature of integration and are readily evaluated if one value of volume on each isobar is known (the saturation volume, for example).

The double integration can be performed graphically from a knowledge of the way in which C_p changes with p and T. This method was used by Jakob[3] whereas Plank[4] attempted to find a formulation for C_p as a function of p and T so that the integration could be performed analytically. Hausen[5] fitted a nine-constant equation to the C_p data of Knoblauch and Koch[6] and from this derived equations for v, H, and S as functions of p and T. The German steam table referred to above was

[1] KNOBLAUCH, O., E. RAISCH, H. HAUSEN, and W. KOCH, "Tabellen und Diagramme für Wasserdampf," R. Oldenbourg, Munich and Berlin, 1932.

[2] See *ibid.* for one method.

[3] JAKOB, M., *Z. Ver. deut. Ing.*, **56**, 1980–1988 (1912).

[4] PLANK, R., *Z. Ver. deut. Ing.*, **60**, 187–193 (1916).

[5] HAUSEN, H., *Forsch. Gebiete Ingenieurw.*, **2**, 319–326 (1931).

[6] KNOBLAUCH, O., and W. KOCH, *Z. Ver. deut. Ing.*, **72**, 1733–1739 (1928).

based on this C_p formulation of Hausen. Theoretically at least, it should be possible to obtain very accurate volumes from C_p data of only moderate accuracy because one is starting with second differentials and proceeding to integral values.

Volume from Enthalpy.—When the enthalpy of a fluid has been directly measured, the volumes may be derived with the aid of Eq. (III.96) as follows:

$$\left(\frac{\partial H}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p \tag{VI.6}$$

$$\frac{v\,dT - T\,dv}{T^2} = \frac{1}{T^2}\left(\frac{\partial H}{\partial p}\right)_T dT \tag{VI.7}$$

$$d\frac{v}{T} = \frac{1}{T^2}\left(\frac{\partial H}{\partial p}\right)_T dT \tag{VI.8}$$

Integrating along an isobar,

$$\frac{v}{T} = \int_{T_0}^{T} \frac{1}{T^2}\left(\frac{\partial H}{\partial p}\right)_T dT + \frac{v_0}{T_0} \tag{VI.9}$$

$(\partial H/\partial p)_T$ is obtained directly from the experimental data and may be expressed as a function of T, either graphically or analytically. Values of v_0 must be known from some independent measurements over the whole range of pressures but only at the single temperature T_0.

Properties from Joule-Thomson Measurements.—The Joule-Thomson effect is considered in detail in the next chapter, but for the present purpose it is sufficient to state that it is the change in temperature which results when a gas is expanded adiabatically from one constant pressure to another in such a way that no external work (other than that of injec-

Fig. VI.8.—Isenthalpic curves.

tion and ejection) is done and no net conversion of internal energy to kinetic energy of mass motion occurs. From such measurements one can derive specific volumes, specific heats, and enthalpies. This method eliminates the necessity for direct measurement of volume and of mass, which are quite troublesome to determine accurately; on the other hand, it involves difficulties of its own in the measurement of the mean temperature of a flowing gas stream and in the maintenance of adiabatic conditions. One cannot say whether or not this method of determining

thermodynamic properties is any better than direct specific-volume measurement but it is at least an important alternative.

From the Joule-Thomson measurements one obtains either directly a set of Tp curves at constant H as shown in Fig. VI.8 or a set of values of μ, the Joule-Thomson coefficient as a function of pressure and temperature from which the Tp curves can be derived by integration. The value of H for each Tp curve is obtained by extrapolation to the $p = 0$ axis, and along this axis we can apply the relation

$$H = H_0 + \int_{T_0}^{T} C_p \, dT \tag{VI.10}$$

Knowing the specific heat at low pressure as a function of temperature and having chosen the arbitrary value of H_0, we can assign a value of H to each point where the pT curve intersects the $p = 0$ axis. Now, for short temperature intervals we can write

$$C_p = \left(\frac{\Delta H}{\Delta T}\right)_p \tag{VI.11}$$

and consider this to be the C_p at the mean temperature. Then

$$\frac{C_p}{C_{p^\circ}} = \frac{(\Delta H/\Delta T)_p}{(\Delta H/\Delta T)_{p^\circ}} \tag{VI.12}$$

and since the ΔH's are the same at all points between any two constant H lines such as H_1 and H_2 in Fig. VI.8, then we have

$$\frac{C_p}{C_{p^\circ}} = \frac{\Delta T_{p^\circ}}{\Delta T_p} \tag{VI.13}$$

We can obtain ΔT_{p° and ΔT_p directly from the plot as shown in Fig. VI.8. If we know C_{p°, we can readily obtain C_p at various temperatures and pressures. Further details on the application of these methods may be obtained by reference to papers by Keenan[1] and Roebuck.[2]

Since

$$-\left(\frac{\partial C_p}{\partial p}\right)_T = \frac{\partial^2 H}{\partial T \, \partial p} = \left[\frac{\partial(\mu C_p)}{\partial T}\right]_p$$

one can write

$$-\left(\frac{\partial C_p}{\partial p}\right)_T = \mu\left(\frac{\partial C_p}{\partial T}\right)_p + C_p\left(\frac{\partial \mu}{\partial T}\right)_p \tag{VI.14}$$

Sage, Kennedy, and Lacey[3] have applied this equation to the calculation of specific heat of propane under pressure from Joule-Thomson data. Since the variables cannot be separated to perform a straightforward integration, it must be done by successive approximations.

[1] KEENAN, J. H., *Mech. Eng.*, **48**, 144–160 (1926).
[2] ROEBUCK, J. R., *Proc. Am. Acad. Arts Sci.*, **60**, 537–596 (1925); **64**, 287 (1930).
[3] SAGE, B. H., E. R. KENNEDY, and W. N. LACEY, *Ind. Eng. Chem.*, **28**, 601 (1936).

Specific volumes may be obtained from Joule-Thomson measurements by the following procedure, once C_p and μ as functions of p and T have been obtained: From Eq. (III.97),

$$T \left(\frac{\partial v}{\partial T} \right)_p - v = \mu C_p \qquad (VI.15)$$

From this point the procedure is exactly the same as that used for calculating volume from enthalpy measurements, the final equation being

$$\frac{v}{T} = \frac{v_0}{T_0} + \int_{T_0}^{T} \frac{\mu C_p}{T^2} \, dT \qquad (VI.16)$$

This method also requires a separate determination of volume as a function of pressure at the one temperature T_0.

Entropy.—This property cannot be directly measured but is calculated from other properties. In general, it increases with increase in temperature and decreases with increase in pressure at constant temperature. The quantitative relationship is given by the equation

$$dS = C_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T} \right)_p dp \qquad (III.95)$$

which becomes, on integration,

$$S = S_0 + \int_{T_0}^{T} C_p \frac{dT}{T} - \int_{p_0}^{p} \left(\frac{\partial v}{\partial T} \right)_p dp \qquad (VI.17)$$

S_0 is a purely arbitrary value at the state p_0, T_0, unless, of course, the entropy for the substance had already been fixed in some other reference state. (For example, it is fairly common practice to make $S = 0$ at the ice point and 1 atm. pressure.)

For temperatures below the critical temperature, the maximum value of the upper limit in the second integral is, of course, the vapor pressure at the temperature in question. The numerical evaluation of the entropy with the aid of Eq. (VI.17) is entirely analogous to the evaluation of enthalpy by Eq. (VI.1).

It is sometimes convenient to calculate entropies from values of enthalpy already available. Assume that one has a series of H values as a function of p and T either in graphical or tabular form. At constant pressure, Eq. (VI.17) can be put in the form

$$S = S_0 + \int_{T_0}^{T} \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_p dT \qquad (VI.18)$$

If the slopes of the HT isobars are known, this equation can be integrated to give entropy differences along a series of isobars. To obtain absolute

values relative to some chosen datum, it is necessary to have a series of S values at different pressures along one isotherm or the values on the saturated-vapor line.

Figure VI.9, in which is sketched an outline of a temperature-entropy diagram, may help one to visualize the procedure followed in these two methods of calculating entropy as applied over the whole field of super-heated vapor. ACB is the boundary curve, and isobars are designated p_0 to p_4. The first method establishes values of S for various tempera-tures along the isobar p_0 in terms of the initial value S_0 for saturated vapor, which in turn is based on the value S_0' for saturated liquid at p_0, T_0. With the values along p_0 as starting points, one then proceeds along
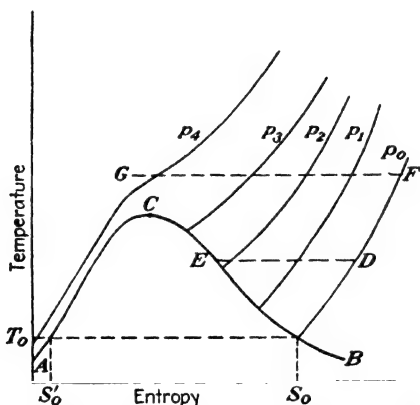
FIG. VI.9.—Calculation of the entropy of superheated vapor.

isotherms, two of which are shown as DE and FG. Below the critical point C, the isotherms all end at the saturated-vapor line.

By the second method one gets entropy values along each isobar in terms of some initial value—for example, the value on the saturated-vapor line that is tied in with S_0' by the entropy change due to vaporiza-tion and the entropy change along the saturated-liquid line. For isobars above the critical one, the tie-in must result either from S values being known along some one isotherm above the critical temperature or by taking as the lower limit T_0 of the integral in Eq. (VI.18) a temperature below critical and relating the entropy to that of the saturated liquid by the known specific volumes of the liquid.

Fugacity.—As shown in Chap. III, the fugacity function is defined by the equations

$$\ln \frac{f}{f^\circ} = \frac{1}{RT} \int_{p^\circ}^{p} v \, dp \qquad \text{(III.140)}$$

and $f^\circ = p^\circ$ as $p^\circ \to 0$

the integration being along an isotherm. From these equations and an equation of state, the numerical value of fugacity is readily obtained.

Illustration 9.—Calculate the fugacity of CO_2 at 50°C. and 100 atm., assuming it to obey the van der Waals' equation of state.

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \qquad \text{(van der Waals' equation)}$$

To evaluate the integral we might proceed to change the independent variable from p to v as was done in Illustration 4, but we shall take this opportunity to illustrate another method. Differentiating the equation of state at constant temperature,

$$dp = -\frac{RT\,dv}{(v - b)^2} + \frac{2a\,dv}{v^3}$$

Then
$$v\,dp = -\frac{RTv\,dv}{(v - b)^2} + \frac{2a}{v^2}\,dv$$

$$\int_{p^0}^{p} v\,dp = \int_{v^\infty}^{v}\left[\frac{2a}{v^2} - \frac{RTv}{(v - b)^2}\right]dv$$

v and v^∞ are the volume limits corresponding to p and p°, respectively. Substituting in Eq. (III.140) and integrating,

$$\ln f - \ln f^\circ = \left[-\frac{2a}{RTv} + \frac{b}{v - b} - \ln\,(v - b)\right]_{v^\infty}^{v}$$
$$= \frac{b}{v - b} - \frac{b}{v^\infty - b} - \frac{2a}{RTv} + \frac{2a}{RTv^\infty} - \ln\,(v - b) + \ln\,(v^\infty - b)$$

As $p \to 0$, $v^\infty \to \infty$, and we may write

$$\frac{1}{v^\infty} = 0 \qquad v^\infty - b = v^\infty = \frac{RT}{p^\circ}$$

Making these substitutions,

$$\ln f - \ln f^\circ = \frac{b}{v - b} - \frac{2a}{RTv} - \ln\,(v - b) + \ln\frac{RT}{p^\circ}$$
$$= \ln\frac{RT}{v - b} + \frac{b}{v - b} - \frac{2a}{RTv} - \ln p^\circ$$

But since, from the definition of fugacity, $f^\circ = p^\circ$ as $p^\circ \to 0$, we finally get

$$\ln f = \ln\frac{RT}{v - b} + \frac{b}{v - b} - \frac{2a}{RTv} \tag{1}$$

From Table IV in the Appendix, $a = 925$, $b = 0.686$ (units are atmospheres, cubic feet, degrees Kelvin, and pound-moles), $R = 1.3145$, $T = 273.2 + 50 = 323.2°K$., v (obtained from the equation of state by a trial solution) $= 1.69$. Substituting in Eq. (1),

$$\ln f = 4.153 \qquad f = 63.1 \text{ atm.}$$

This is, of course, only an approximate result since the van der Waals' equation is only an approximation to the pvT behavior of CO_2. It happens, however, that the approximation is a very good one in this case, as will be seen in a moment when a more accurate equation of state is used.

The Beattie-Bridgeman equation of state gives the following equation for fugacity:

$$\ln f = \ln \frac{RT}{v} + \frac{2\beta}{RTv} + \frac{3\gamma}{2RTv^2} + \frac{4\delta}{3RTv^3} \tag{2}$$

(For the definitions of β, γ, and δ, see page 183.) For the same numerical case as above, this equation gives $f = 62.1$.

Lewis and Randall[1] developed the following useful approximate method for the calculation of fugacity. In Eq. (III.142) for the definition of fugacity, *viz.*,

$$\ln \frac{f}{p} = -\frac{1}{RT} \int_0^p \alpha \, dp$$

assume α is a constant and integrate, obtaining

$$\frac{f}{p} = e^{-\frac{\alpha p}{RT}} \tag{VI.19}$$

For values of $\alpha p/RT$ that are small relative to unity, the right-hand side of this equation reduces to

$$1 - \frac{\alpha p}{RT} = \frac{pv}{RT}$$

and finally
$$f = \frac{p^2 v}{RT} \tag{VI.20}$$

It should be remembered that this is good only at relatively low pressures.

Thermodynamic Properties from Compressibility Data by Graphical Methods.—When accurate values of thermodynamic properties are to be obtained over wide ranges of conditions, the use of an ordinary equation of state is generally unsatisfactory because none of the usual equations is sufficiently accurate over wide ranges to permit accurate determination of first- (to say nothing of second-) differential coefficients. Recourse must then be had to the use of graphical methods operating on the original data. The following brief discussion of such methods is based mainly on a series of papers by Deming and Shupe,[2] who calculated various thermodynamic properties for hydrogen, nitrogen, and carbon monoxide from the compressibility data.

In the calculation of S, H, C_p, μ, etc., when p and T are the independent variables, the coefficients $(\partial v/\partial T)_p$ and $(\partial^2 v/\partial T^2)_p$ must be evaluated. When v is plotted against T, the curve obtained is nearly linear and a direct determination of the slope at various temperatures

[1] Lewis, G. N., and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," p. 197, McGraw-Hill Book Company, Inc., 1923.
[2] Deming, W. E., and L. E. Shupe, *Phys. Rev.*, **37**, 638–654 (1931): **38**, 2245–2264 (1931); **40**, 848–859 (1932).

cannot be made with any accuracy. If, however, one plots, not v itself, but some residual quantity or correction term, the slope will be greatly magnified and can easily be determined accurately. Deming and Shupe used two residual quantities, *viz.*,

$$\alpha = \frac{RT}{p} - v \tag{VI.21}$$

$$\Delta = v\left(\frac{pv}{RT} - 1\right) \tag{VI.22}$$

From the definition of the ideal gas, it is clear that both these quantities would be zero for such a gas, and so they are essentially correction factors for departure from the ideal state. From them the following equations are obtained by differentiation:

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} - \left(\frac{\partial \alpha}{\partial T}\right)_p \tag{VI.23}$$

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = -\left(\frac{\partial^2 \alpha}{\partial T^2}\right)_p \tag{VI.24}$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{(pv/RT)(v/T) + (\partial\Delta/\partial T)_p}{1 + (2\Delta/v)} \tag{VI.25}$$

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = \frac{1}{(2\Delta/v) + 1} \left\{ \left(\frac{\partial^2\Delta}{\partial T^2}\right)_p - \frac{2p}{RT} \frac{[(\Delta/T) - (\partial\Delta/\partial T)_p]^2}{[(2\Delta/v) + 1]^2} \right\} \tag{VI.26}$$

All graphical measurements are obtained by operating on the residual quantities rather than on the original data. Figure VI.10 shows the great difference between the curvature of v vs. T, Δ vs. T, and α vs. T.

The usual differential equations for the thermodynamic properties are readily transformed to forms involving α or Δ by use of the relations given above. The following are two typical ones:

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial \alpha}{\partial T}\right)_p - \alpha \tag{VI.27}$$

$$\mu = \frac{\alpha - T(\partial\alpha/\partial T)_p}{C_p} \tag{VI.28}$$

Deming and Shupe smoothed the original data by means of the Δ and α plots. In some cases the graphical differentiations were checked by fitting equations to the curves. It is also interesting to note that they commonly used

$$-\frac{p}{v}\left(\frac{\partial v}{\partial p}\right)_T \qquad \text{and} \qquad \frac{T}{v}\left(\frac{\partial v}{\partial T}\right)_p$$

instead of the derivatives alone because these functions are dimensionless and also because they are equal to unity for an ideal gas and hence one sees at a glance the extent of departure from ideality.

It is not practicable to illustrate this method in detail, but the following outline may be useful. Assume that it is desired to calculate the enthalpy of methane as a function of pressure and temperature. Kvalnes and Gaddy[1] have tabulated values of the Amagat compressibility factor A for pressures of 1 to 1,000 atm. and temperatures of -70 to 200°C. From these, values of specific volume v are readily calculated and then values of α using Eq. (VI.21). Isobars of α vs. T may then be
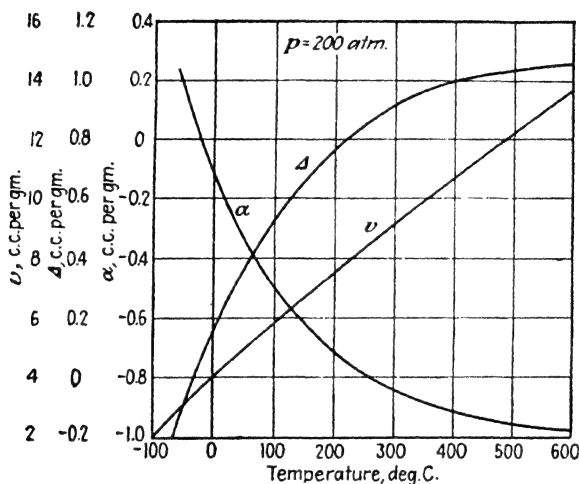
Fig. VI.10—Comparison of the curvature of graphs of v, α, and Δ vs. the temperature at constant pressure   [*Data for nitrogen of Deming and Shupe, Phys. Rev.*, **37**, 638 (1931).]

plotted, from which the slopes $(\partial\alpha/\partial T)_p$ are then obtained by graphical differentiation and finally tabulated as a function of both p and T. From Eq. (VI.27) we have

$$H = H_0 + \int_{p^0}^{p}\left[T\left(\frac{\partial\alpha}{\partial T}\right)_p - \alpha \right] dp$$

To take a specific case, assume it is desired to obtain H at 100°C. and 200 atm., given that H is to be zero at 0°C. and 1 atm. Values of α and of $(\partial\alpha/\partial T)_p$ for various pressures along the 100°C. isotherm would be read from the table previously prepared and the quantity

$$T\left(\frac{\partial\alpha}{\partial T}\right)_p - \alpha$$

calculated. This quantity is then plotted against pressure, and the area under the curve between the two given pressure limits is equal to the above integral in mechanical-energy units. This value is converted to

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[1] Kvalnes, A. M., and V. L. Gaddy, *J. Am. Chem. Soc.*, **53**, 397–399 (1931).

thermal units and added to the integration constant H_0, whose value is given by

$$H_0 = \int_{273.2}^{373.2} C_{p^\circ} \, dT$$

where C_{p° is the specific heat at 1 atm.

This is, of course, too long and tedious a process to use if only a few values of enthalpy are desired. It is very useful, however, when a thermodynamic diagram or table of properties covering a considerable field is to be prepared. Edmister[1] has calculated C_p, $C_p - C_v$, μ, S, and H for methane in this way and tabulated the values at a series of temperatures and pressures.

Calculation of the fugacity through use of the residual α is the method originally introduced by Lewis and Randall and used by many subsequent workers. Thus, from the definition of f and α,

$$\ln f = \ln p - \frac{1}{RT} \int_0^p \alpha \, dp \qquad \text{(VI.29)}$$

α vs. p isotherms are plotted and extrapolated to $p = 0$, and the area under the curve gives the value of the integral.

Another method for the calculation of isothermal changes in thermodynamic properties based on the use of residuals is given by York.[2] The residual employed is the deviation from the linear-isometric relation. The original paper must be consulted for details.

Generalized Thermodynamic Properties.—In Chap. V it was shown that the volume of any gas or vapor could be conveniently represented on a generalized compressibility-factor chart by graphing the compressibility factor C $(= pv/RT)$ against reduced pressure p_R $(= p/p_c)$ with reduced temperature T_R $(= T/T_c)$ as parameter. In this way the approximate behavior of all gases could be represented on a single chart. An equation that would express C as a function of p_R and T_R would be a generalized equation of state. From such a chart or from the corresponding equations, the various thermodynamic properties such as f, H, and S may be calculated.

Thus Eq. (III.140) may be changed to

$$\log \frac{f}{f^\circ} = \int_{p^\circ}^p C \, d \log p \qquad \text{(VI.30)}$$

Values of C may be read from the chart for various values of p_R at a given T_R and plotted against $\log p$. The area under the curve down to some definite pressure such as $p^\circ = 1$ atm. or $p^\circ = 0.1$ atm. gives the value of $\log f/f^\circ$, and assuming that $f^\circ = p^\circ$ one gets the value of f.

[1] EDMISTER, W. C., *Ind. Eng. Chem.*, **28**, 1112–1116 (1936).
[2] YORK, R., *Ind. Eng. Chem.*, **32**, 54–56 (1940).

It one wished to be more rigorous, he would go to the limit of $p° = 0$, but as $p° \to 0$, the value of the integral becomes indeterminate. This difficulty can be avoided by subtracting $\int_{p°}^{p} \frac{dp}{p}$ from both sides of Eq. (VI.30) and putting $p° = f°$, giving

$$\ln f = \log_{10} p + \frac{1}{2.303} \int_{p°}^{p} \frac{C - 1}{p} \, dp \qquad (VI.31)$$

It can readily be shown that $(C - 1)/p$ approaches a finite value as $p \to 0$.

Illustration 10.—Calculate the fugacity of CO_2 at 50°C. and 100 atm., using the compressibility-factor chart.

$$T_R = \frac{323.1}{304.1} = 1.062 \qquad p_R \text{ (100 atm.)} = \frac{100}{73.0} = 1.37$$

Reading values of C from Fig. V.2 we may make the following tabulation:

p, atm.	p_R	C	$\dfrac{C - 1}{p}$
1	0.0137		
5	0.0685	0.990	−0.002
10	0.137	0.970	−0.003
20	0.274	0.930	−0.0035
30	0.411	0.885	−0.0042
40	0.548	0.830	−0.00425
50	0.685	0.770	−0.0046
60	0.823	0.710	−0.00484
70	0.960	0.650	−0.0050
80	1.095	0.600	−0.0050
90	1.233	0.525	−0.00527
100	1.370	0.430	−0.0057

From a plot of $(C - 1)/p$ vs. p we find the area under the curve between $p = 100$ and $p = 0$ to be −0.44.

From Eq. (VI.31), $2.303 \log_{10} f = 2.303 \log_{10} 100 - 0.44$
$$= 1.807$$
$$f = 64.2 \text{ atm.}$$

The dimensionless ratio f/p, termed "activity coefficient" by Newton[1] from its analogy to the same term used by Lewis and Randall for liquid solutions, has been shown to be a function of p_R and T_R.   Newton calculated the fugacity for a large number of substances by a graphical method

[1] NEWTON, R. H., *Ind. Eng. Chem.*, **27**, 302 (1935).

from the pvT data and expressed the averaged results in three charts, reproduced here as Figs. VI.11 to VI.13. From these figures the activity
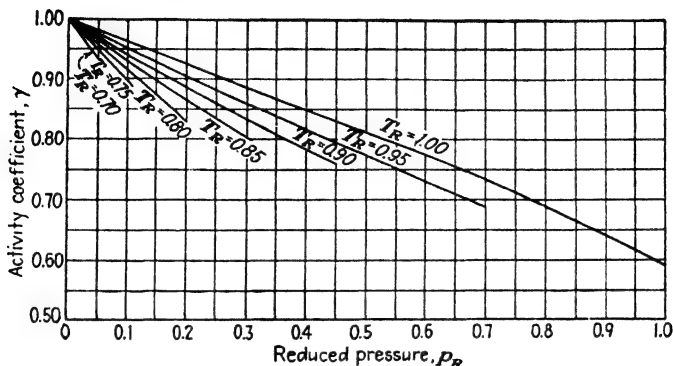
FIG. VI.11.—Activity coefficients of pure gases. I. Low-pressure range. [*Reproduced from R. H. Newton, Ind. Eng. Chem.*, **27**, 302 (1935).]
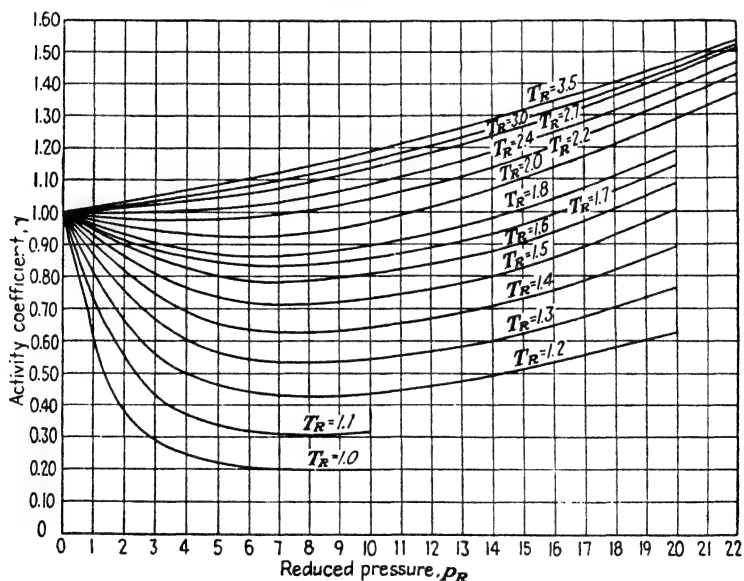
FIG. VI.12.—Activity coefficients of pure gases. II. Intermediate-pressure range. [*Reproduced from R. H. Newton, Ind. Eng. Chem.*, **27**, 32 (1935).]

coefficient γ, and hence the fugacity, can be easily obtained under almost any condition for a substance whose critical data are known.

From the definition of f and of C we have, at constant T,

$$d \ln f = C d \ln p$$

Subtracting $d \ln p$ from both sides and noting that $p = p_c p_R$, one gets

$$\ln \frac{f}{p} = \ln \gamma = \int_{p_R}^{p_R^\circ} (C - 1) d \ln p_R \qquad \text{(VI.32)}$$

p_R° is the reduced pressure in the standard state where gases may be assumed ideal. With the aid of this equation, the activity coefficient
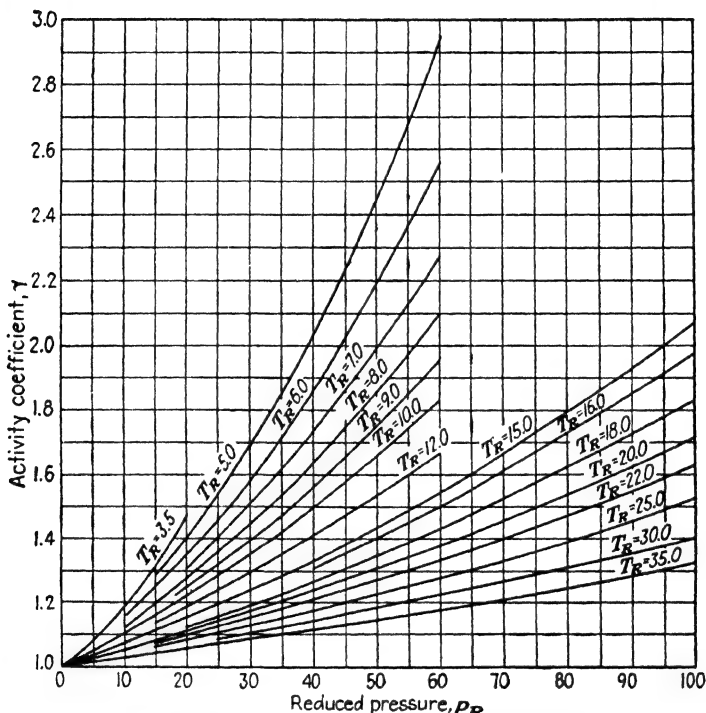
Fig. VI.13.—Activity coefficients of pure gases. III. High-pressure range. [*Reproduced from R. H. Newton, Ind. Eng. Chem.*, **27**, 302 (1935).]

can be obtained as a function of p_R and T_R from the generalized compressibility-factor chart. This is the method used by Watson and Smith,[1] who performed the integration graphically.

In a similar manner the effect of pressure on other properties can be approximated from the generalized compressibility-factor data. For example, Eq. (III.96) for the case of constant temperature may be put in the form

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{RT^2}{p} \left(\frac{\partial C}{\partial T}\right)_p \qquad \text{(VI.33)}$$

[1] WATSON, K. M., and R. L. SMITH, *Nat. Petroleum News*, July, 1936.

and this may be integrated with the aid of C values obtained from a generalized compressibility-factor chart.

Cope, Lewis, and Weber,[1] and Lewis and Luke[2] represent C for hydrocarbons as a function of p_R and T_R by a part algebraic and part graphical relation and from it obtain equations for H and E as a function of pressure. These equations are complex, and their solution is simplified by giving certain functions in graphical form.

Watson and Nelson[3] derive relatively simple equations for C as a function of p_R and T_R for hydrocarbons over a limited range and use
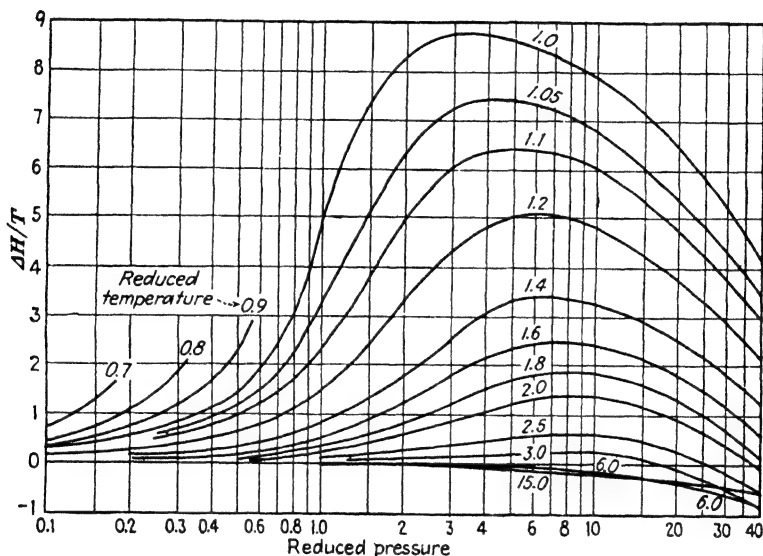
Fig. VI.14.—Generalized enthalpy-difference chart. ΔH = difference between enthalpy at atmospheric pressure and that at an elevated pressure along an isotherm, B.t.u., per lb.-mole. T is in degrees Rankine. (*Reproduced from Watson and Smith, Nat. Petroleum News, July* 1, 1936.)

these equations of state to integrate Eq. (VI.33), finally presenting the results in a plot of $(H° - H)/T$ vs. p_R at various values of T_R.

Such a graph provides a very simple means of obtaining the approximate enthalpy of any substance whose critical pressure and temperature are known. Figure VI.14 gives a graph of this type, which was obtained by Watson and Smith[4] as follows:

[1] COPE, J. Q., W. K. LEWIS, and H. C. WEBER, *Ind. Eng. Chem.*, **23**, 887 (1931).
[2] LEWIS, W. K., and C. D. LUKE, *Trans. A.S.M.E.* (P.M.E.-54-8), 55-61 (1932).
[3] WATSON, K. M., and E. F. NELSON, *Ind. Eng. Chem.*, **25**, 880-887 (1933).
[4] *Loc. cit.*

$$\left(\frac{\partial \ln f}{\partial T}\right)_p = \frac{H^\circ - H}{RT^2}$$

$$= \frac{\Delta H^\circ}{RT^2} \qquad \text{(III.146)}$$

H is the molal enthalpy at any given p and T. H° is the molal enthalpy at the same T but at the standard low pressure p°, where the gas is ideal and H does not change with pressure. Since $f = \gamma p$,

$$\left(\frac{\partial \ln f}{\partial T}\right)_p = \left(\frac{\partial \ln \gamma}{\partial T}\right)_p$$

and since $T = T_R T_c$,

$$\frac{\Delta H^\circ}{T} = RT_R T_c \left(\frac{\partial \ln \gamma}{T_c \, \partial T_R}\right)_p \qquad \text{(VI.34)}$$

$$\frac{\Delta H^\circ}{T} = R \left(\frac{\partial \ln \gamma}{\partial \ln T_R}\right)_{p_R} \qquad \text{(VI.35)}$$

Values of the slope were obtained by graphical differentiation on a plot of γ vs. T_R with p_R as parameter.

Illustration 11.—What is the difference between the enthalpy of 1 lb. of steam at 1,200 lb. per sq. in. abs. and 800°F. and that at the same temperature but low pressure?

$$T_R = \frac{800 + 459.7}{1,165} = 1.081$$

$$p_R = \frac{1,200}{218.2 \times 14.7} = 0.374$$

From Fig. VI.14,

$$\frac{\Delta H M}{T} = 0.85$$

$$\Delta H \text{ (B.t.u./lb.)} = \frac{0.85 \times 1,259.7}{18} = 59.5$$

The corresponding value from the Keenan-Keyes steam table is 53.5. This is a good check considering the approximations involved in Fig. VI.14 and the generally abnormal behavior of water vapor.

Other thermodynamic properties may be generalized in an analogous manner. Thus the following equations are readily derived by rigorous thermodynamic methods:

$$C_{p^\circ} - C_p = \frac{H^\circ - H}{T} + \left\{\frac{\partial[(H^\circ - H)/T]}{\partial \ln T_R}\right\}_{p_R} \qquad \text{(VI.36)}$$

and

$$\mu C_p = \frac{T_c T_R}{p_c} \left\{\frac{\partial[(H^\circ - H)/T]}{\partial p_R}\right\}_{T_R} \qquad \text{(VI.37)}$$

With the aid of Fig. VI.14 and if the critical p and T are known, it is clear that the specific heat and the Joule-Thomson coefficient can be

obtained for elevated pressures. Watson and Smith[1] applied these equations and gave the results in the form of graphs for convenient use.

Dodge[2] generalized the effect of pressure on specific heat by plotting C_p/C_p^o, the ratio of the specific heat at any pressure to that at a low pressure approaching zero, both at the same temperature, vs. the reduced pressure with reduced temperature as parameter. Watson and Smith[3] treated $C_p - C_p^o$ in the same way, and their graph is reproduced in Fig.
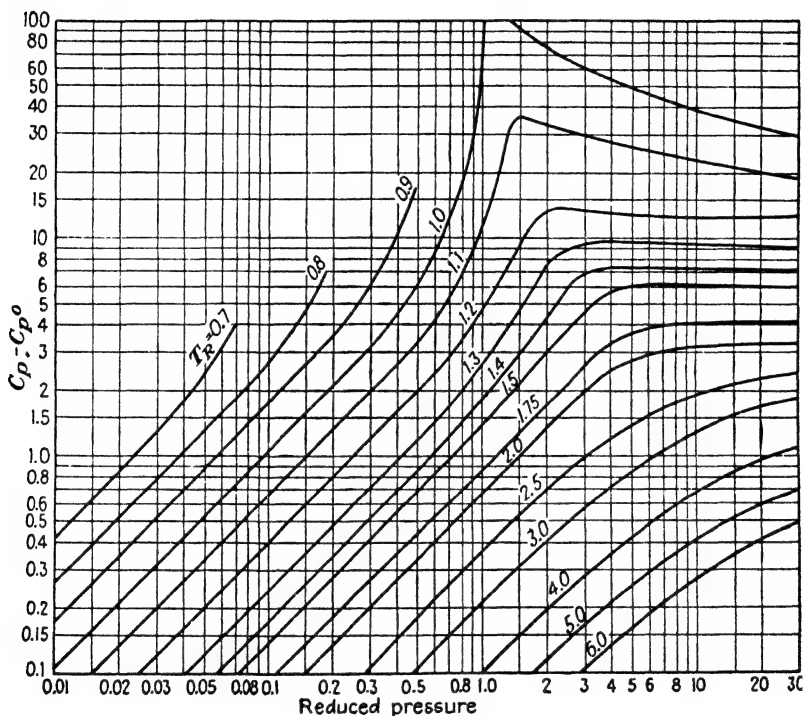
Fig. VI.15.—Generalized chart for effect of pressure on molal heat capacity at constant pressure. (*Reproduced from Watson and Smith, Nat. Petroleum News, July 1, 1936.*)

VI.15 since it is somewhat more convenient to use than that of Dodge. Good data for testing such a correlation are not very abundant, but it would appear that this plot is not so reliable as the corresponding one for compressibility factor. Deviations of 25 per cent or more from "observed"[4] values are not uncommon. On the other hand, it is to be

[1] *Loc. cit.*

[2] DODGE, B. F., *Ind. Eng. Chem.*, **24**, 1353 (1932).

[3] WATSON, K. M., and R. L. SMITH, *loc. cit.*

[4] Direct experimental measurements are very few in number. "Observed" generally means a value calculated in some other way such as by an equation of state.

noted that the pressure effect is not great, and a considerable error in ΔC_p can be made without a great effect on C_p.

Illustration 12.—Estimate the constant-pressure molal heat capacity of methane at 2,000 lb. per sq. in. and 100°F.; of nitrogen at 4,000 lb. per sq. in. and 100°F.; of CO₂ at 2,000 lb. per sq. in. and 250°F.; and of hydrogen at 0°F. and 5,000 lb. per sq. in.

The solution is presented in the following tabulation:

Gas	Reduced pressure	Reduced temp.	$C_p - C_{p^o}$ from Fig. VI.15	C_{p^o}	C_p	C_p "observed"
CH₄	2.96	1.63	3.6	8.79	12.4	12.17
N₂	8.1	2.46	1.8	6.96	8.8	9.05
CO₂	1.87	1.30	6.5	10.14	16.6	16.20
H₂	26.6	13.8	0.1	6.79	6.9	7.16

Units of C_p are B.t.u. per lb.-mole per °F.

Values of C_{p^o} and "observed" C_p were taken from *Cornell Univ. Eng. Expt. Sta. Bull.* 30, October, 1942.

Another method of generalizing thermodynamic properties with particular reference to hydrocarbons was given by Edmister.[1] This is based on a reduced equation of state in graphical form, utilizing the reduced residual quantity α_R defined by the equation

$$\alpha_R = \frac{\alpha}{\alpha_c}$$

where α is defined by Eq. (VI.21).   The latter equation may be rearranged to

$$\frac{v}{\alpha_c} = \frac{RT_cT_R}{p_c\alpha_c p_R} - \alpha_R \qquad (VI.38)$$

The ratio $RT_c/p_c\alpha_c$ is dimensionless and is nearly constant at the value 1.37 for all hydrocarbons.   Equation (VI.38) combined with a graph of α_R vs. p_R with parameters of T_R furnishes a basis for the calculation of the thermodynamic properties.   Such a graph, based on the published pvT data of nine hydrocarbons, is given in Edmister's paper.   The method of calculating the effect of pressure on the properties may be briefly illustrated by considering the case of enthalpy.   From Eqs. (VI.1) and (VI.38) we have, at constant temperature,

$$\Delta H = -p_c\alpha_c \int_0^{p_R} \left[\alpha_R - T_R \left(\frac{\partial \alpha_R}{\partial T_R}\right)_{p_R} \right] dp_R \qquad (VI.39)$$

Such values may not, themselves, be very accurate, since it is often necessary to extrapolate the equation of state.

[1] EDMISTER, W. C., *Ind. Eng. Chem.*, **30,** 352–358 (1938).

The integration may be performed graphically, using values of α_R read from the graph. Edmister gives an extensive table of "reduced thermodynamic functions" from which the fugacity, specific heat, enthalpy, and entropy of any hydrocarbon can be obtained whose critical pressure and temperature are known.

Maron and Turnbull[1] have recently reviewed the various methods for generalized properties and have presented generalized analytical correlations based on the Beattie equation of state and on an empirical equation of state of the form of Eq. (V.31). Briefly, their method consists in eliminating p and T from a volume-explicit equation in terms of p_c, p_R, T_c and T_R and then evaluating the constants that are characteristic of a particular gas by the data for nitrogen. From this procedure there results a generalized equation that should be good for any gas within the limits of accuracy of the theorem of corresponding states. Several examples are worked out in detail in their paper.

Properties of Solutions.—It is not feasible to enter into any detailed consideration of this very large subject, and we shall limit our discussion to a mere recital of some of the available methods. If an equation of state for the mixture can be developed along the lines indicated in Chap. V, various properties such as H, S, and f can be calculated by methods similar to those illustrated in this chapter for the case of single components. This method is rigorous, and the accuracy of the results will depend only on how well the equation of state represents the volumetric behavior of the mixture.

An empirical method that is sufficiently good for many cases is to find the pseudocritical pressure and temperature of the mixture and then treat the mixture as a pure component having this critical state. The methods of obtaining the properties in this way through the application of the theorem of corresponding states was illustrated earlier in this chapter.

Sage, Olds, and Lacey[2] have developed a method for calculating the enthalpy of gaseous hydrocarbon mixtures which consists in treating the mixture as a four-component system composed of methane, ethane, n-butane, and n-pentane. The enthalpy of a mixture is calculated from the usual equation relating it to the partial enthalpies of the various components [Eq. (IV.8)], the latter quantities being obtained from tabulated experimental data on the partial enthalpies in binary solutions. This method of calculation was compared with experimental measurements on two natural gases and with calculated values based on the pseudocritical constants and the law of corresponding states. Their

[1] MARON, S. H., and D. TURNBULL, *Ind. Eng. Chem.*, **34**, 544 (1942).

[2] SAGE, B. H., R. H. OLDS, and W. N. LACEY, Preprint for Twenty-third Annual Meeting of the A.P.I., Nov. 8, 1942.

method gave somewhat closer agreement with the experimental data than the latter method, but it seems doubtful if the gain is sufficient to justify the greater complexity of the method.

THE TWO-PHASE REGION

The discussion will be confined largely to the case of liquid-vapor equilibrium, but it should be noted that most of the general relationships apply equally well to liquid-solid, solid-vapor, and solid-solid equilibria.

The region we are discussing is bounded in pressure and temperature by the triple point on the low side and the critical point on the high side (see Fig. VI.1). It is shown as region VII in Fig. VI.2.

Volume, Enthalpy, and Entropy.—Any point in this region represents a mixture of saturated vapor and saturated liquid; and since these three properties are all extensive, their values for a mixture are merely the sums of the individual values for the two phases. Thus we have

$$v = v' + x(v'' - v') \tag{VI.40}$$

$$H = H' + x(H'' - H') \tag{VI.41}$$

$$H = H' + xL \tag{VI.42}$$

$$S = S' + x(S'' - S') \tag{VI.43}$$

$$S = S' + x\frac{L}{T} \tag{VI.44}$$

where x is the quality, *i.e.*, fraction of the mixture that is present as vapor. Values for saturated vapor ['''] may be regarded simply as the limiting values of the properties in the superheated region when the pressure is equal to the vapor pressure for the given temperature or the temperature equals the boiling point for the pressure in question. Similarly, the values for saturated liquid ['] are the limiting values for the liquid region when the liquid is at its boiling point. From Eq. (VI.43) it is evident that the quality at any point in the two-phase region of a TS diagram is simply the horizontal distance from the point to the liquid line divided by the total horizontal distance between the two boundary curves. This is the basis for drawing the quality lines on such a diagram.

The internal energy is obviously given by the equation

$$\begin{aligned}
E &= H - pv \\
&= H' - pv' + x[(H'' - H') - p(v'' - v')] \tag{VI.45}
\end{aligned}$$

Vapor-pressure Relationships.—The vapor pressure as a function of the temperature is one of the most important of the thermodynamic properties and must be determined experimentally. In interpolating and extrapolating the experimental data and also in reducing the required data to a minimum, vapor-pressure equations are very useful, and we shall proceed to review some of the most important of them. The

starting point for most vapor-pressure equations is the Clausius-Clapeyron equation; in its differential form [Eq. (IV.153)] this is entirely rigorous, but various assumptions are introduced to integrate it.
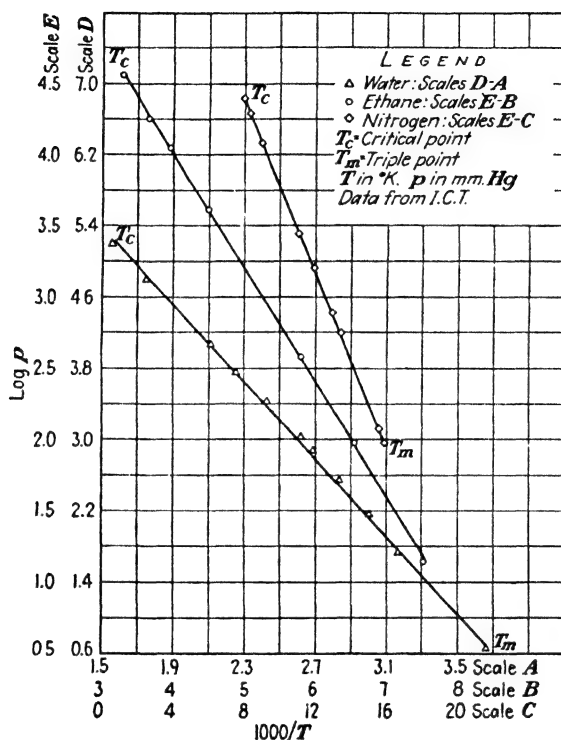
Fig. VI.16.—Illustration of linear log p vs. $1/T$ vapor-pressure relationship.

Linear log p vs. 1/T.—Neglecting the volume of liquid in comparison with that of the vapor and assuming that the vapor is an ideal gas, Eq. (IV.153) becomes

$$\frac{d \ln p}{dT} = \frac{L}{RT^2} \qquad \text{(VI.46)}$$

Integrating on the assumption that L is independent of the temperature,

$$\ln p = -\frac{L}{RT} + I \qquad \text{(VI.47)}$$

or we may write as an empirical equation

$$\log p = \frac{A}{T} + B \qquad \text{(VI.48)}$$

This is an exceedingly useful equation, for it fits the vapor-pressure data for practically all substances over rather wide ranges with reasonable accuracy and only two experimental values are needed to determine the constants. Figure VI.16 shows how well the measured vapor pressures of water, ethane, and nitrogen agree with this simple relationship. The agreement for nitrogen is almost perfect over the entire range of the liquid phase. This is quite remarkable in view of the fact that no one of the three assumptions on which the equation is based is even approximately valid over such a range. Copson and Frolich[1] have presented a chart of the vapor pressures of eight of the lower hydrocarbons over the range from about 0.001 atm. to the critical pressure, using coordinates of $\log p$ and $1/T$, and the departure from straight lines was small.

Other Equations.—Assuming the latent heat of vaporization to be related to the temperature by the equation

$$L = L_0 + aT \tag{VI.49}$$

integration of Eq. (VI.46) gives the following useful empirical equation for vapor pressure:

$$\log p = \frac{A}{T} + B \log T + C \tag{VI.50}$$

The vapor-pressure equation to use in any given case depends entirely on the particular substance and on the accuracy desired, and no general rules can be given. The following are some equations that have been used to represent vapor-pressure data:

$$\log p = \frac{A}{T} + B + CT + DT^2 + \cdots \tag{VI.51}$$

$$\log p = \frac{A}{T} + B + 1.75 \log T + CT \tag{VI.52}$$

$$\log p = \frac{A}{T} + B + C \log T + DT + \cdots \tag{VI.53}$$

$$\log \frac{p_c}{p} = a\left(\frac{T_c}{T} - 1\right) \tag{VI.54}$$

$$\log \frac{p_c}{p} = \frac{T_c - T}{T}\left[\frac{a + b(T_c - T) + c(T_c - T)^3 + e(T_c - T)^4}{1 + d(T_c - T)}\right] \tag{VI.55}$$

$$\log p = \frac{T - T_B}{T}\left[A - B\left(\frac{T - T_B}{T_B}\right) + C\left(\frac{T - T_B}{T_B}\right)^2\right] \tag{VI.56}$$

Equation (VI.52) is commonly known as the "Nernst formula"; Eq. (VI.55) was used by Smith, Keyes, and Gerry[2] to represent with extreme

[1] COPSON, R. L., and P. K. FROLICH, *Ind. Eng. Chem.*, **21**, 1116–1117 (1929).

[2] SMITH, L. B., F. G. KEYES, and H. T. GERRY, *Proc. Am. Acad. Arts Sci.*, **69**, 137–168 (1934).

accuracy their data on water from the normal boiling point to the critical point; Eq. (VI.54) is an equation proposed by van der Waals.

Dühring's Rule.—This rule furnishes a simple and reasonably accurate method of interpolating and extrapolating vapor pressures. The rule is expressed by the equation

$$\frac{t_{A_1} - t_{A_2}}{t_{B_1} - t_{B_2}} = c \qquad \text{(VI.57)}$$

where t_{A_1} and t_{B_1} are corresponding boiling points of substances A and B, that is, boiling points under the same pressure p_1, t_{A_2} and t_{B_2} are the same for some other pressure p_2, and c is a constant. A is the substance the vapor pressure of which is to be determined, and B is a reference substance the vapor pressure of which is known over the desired range and which should, if possible, be chemically similar to A. Two vapor pressures of the substance A are needed to evaluate c. Equation (VI.57) can also be put in the form

$$t_A = k_1 t_B + k_2 \qquad \text{(VI.58)}$$

where t_A and t_B are any corresponding boiling points of substances A and B. From this form of the equation it can be seen that t_A plotted against t_B yields a straight line, and the rule is generally used in this graphical form. In whatever form the rule is used, it is somewhat inconvenient in that it is not self-contained but must be used in conjunction with a vapor-pressure curve or table for the reference substance. In the absence of specific data bearing on the point it must be questioned whether this rule has any advantage over the use of the linear log p vs. $1/T$ equation.

Roehl[1] has extended the usefulness of the rule by showing how the two constants k_1 and k_2 can be simply related to the concentration in the case of aqueous solutions and to the number of carbon atoms in the case of a homologous organic series.

Cox Chart.—Cox[2] introduced a method of plotting vapor-pressure data that gives straight lines and also permits the determination of the entire vapor-pressure curve from a single experimental point in some instances. His method consists in laying off on the ordinate of a pair of ordinary coordinate axes a scale of logarithms of pressure and then drawing the horizontal coordinate lines. A straight line is then drawn near the center of the sheet sloping upward to the right at an angle of about 45 deg. with the horizontal. This line is chosen to be the vapor-pressure curve of a reference substance, generally water (or mercury for temperatures above the critical of water). With the aid of the vapor·

[1] Roehl, E. J., *Ind. Eng. Chem.*, **30**, 1320–1322 (1938).
[2] Cox, E. R., *Ind. Eng. Chem.*, **15**, 592 (1923).

pressure data on water a scale of temperatures is then plotted along the abscissa to conform to the arbitrarily chosen vapor-pressure line and the vertical coordinate lines are drawn. When the vapor pressure of any substance is plotted on this system of coordinates, it is found to yield approximately a straight line. Furthermore, groups of related compounds such as paraffin hydrocarbons, alcohols, and metals give lines that converge to a common point. This means that the entire vapor-pressure line of a member of such a group for which the point of convergence is known could be determined from a single value of the vapor pressure, for example, the normal boiling point.

It has been shown by Calingaert and Davis[1] that the use of the Cox chart is equivalent to using the following equation to represent the vapor pressure–temperature relationship:

$$\log p = A - \frac{B}{t + 230} \tag{VI.59}$$

where A and B are empirical constants and t is in degrees centigrade. It is clear that a straight line would result from plotting $\log p$ vs. $1/(t + 230)$ and two experimental points suffice to determine the line. This is essentially the same as using the linear $\log p$ vs. $1/T$ relationship [Eq. (VI.48)] except that an empirical value of 230 is chosen to represent the ice point on the centigrade absolute scale.

Latent Heat of Vaporization.—If the vapor pressure of the substance in question, as well as the specific volume of both the saturated liquid and vapor, is known, the latent heat can be exactly determined from Eq. (IV.153).

Illustration 13.—Measurements of the vapor pressure of methane by Keyes, Taylor, and Smith[2] were represented by the equation

$$\log p \text{ (atm.)} = -\frac{595.546}{T} + 8.09938 - 4.04175 \times 10^{-3}T$$
$$+ 1.68655 \times 10^{-4}T^2 - 2.51715 \times 10^{-7}T^3$$

The specific volumes of vapor and liquid were found to be 34.49 and 3.0496 cc. per g., respectively, at 165°K. Calculate the latent heat at this temperature.

Write the vapor-pressure equation in the general form

$$\log p = \frac{A}{T} + B + CT + DT^2 + ET^3$$

Differentiating,

$$\frac{1}{2.3026} \frac{dp}{p} = \left(-\frac{A}{T^2} + C + 2DT + 3ET^2 \right) dT$$

or

$$\frac{dp}{dT} = 2.3026p \left(-\frac{A}{T^2} + C + 2DT + 3ET^2 \right)$$

[1] Calingaert, G., and D. S. Davis, *Ind. Eng. Chem.*, **17**, 1287–1289 (1925).

[2] Keyes, F. G., Taylor, and L. B. Smith, *J. Math. Phys.*, **1**, 211–242 (1922).

$$T = 165°K., \qquad p = 19.22$$
$$\Delta v = 34.49 - 3.05 = 31.44 \text{ cc./g.}$$
$$\frac{dp}{dT} = 0.73018 \text{ atm./°K.}$$

$$\therefore L = 165 \times 31.44 \times 0.73018 = 3,788 \text{ cc.-atm./g.} \times 0.02420 = 91.68 \text{ g.-cal./g.}$$

If the pressure is low, one might assume that the vapor is an ideal gas and that the liquid volume is negligible and calculate the latent heat by Eq. (VI.46).

Illustration 14.—The vapor pressure of nitrogen is given by the equation

$$\log p \text{ (atm.)} = -\frac{304.494}{T(°K.)} + 3.93352$$

Calculate the latent heat at the normal boiling point.

From the vapor-pressure equation, when $p = 1.000$, $T = 77.41°K$. Writing the equation in the general form,

$$\log p = -\frac{A}{T} + B$$

Then

$$\frac{1}{p}\frac{dp}{dT} = \frac{2.3026A}{T^2}$$

$$= \frac{L}{RT^2} \qquad \text{[by Eq. (VI.46)]}$$

or

$$L = 2.3026AR \qquad (1)$$
$$= 2.3026 \times 304.49 \times 1.987 = 1,393 \text{ cal./g.-mole}$$

The difference between this figure and the observed value of Dana[1] (1,335 cal. per mole) is greater than one would expect on the basis of departure from the gas law. Even greater discrepancies between observed and calculated values have been noted in other cases. For example, the equation

$$\log p_{\text{mm.}} = -\frac{1,992.1}{T} + 8.7764$$

which fits the Ramsay and Young data for the vapor pressure of methanol very well, gives for the latent heat at the normal boiling point, by use of Eq. (VI.46), the value 9,115 cal. per mole whereas the experimental value is 8,420.

These discrepancies illustrate an important point. Although vapor-pressure equations of the linear $\log p$ vs. $1/T$ type may represent the vapor-pressure data quite well, they may not be satisfactory for the calculation of the slope dp/dT. This is indicated by the fact that such a vapor-pressure equation, when coupled with the ideal-gas law, leads to

[1] DANA, L. I., *Proc. Am. Acad. Arts Sci.*, **60**, 241–267 (1927).

Eq. (1) of Illustration 14, which states that the latent heat is independent of temperature, which we know to be quite contrary to fact.

Specific Heats of Saturated Liquid and Vapor.—Specific heat, in general, is defined by the equation

$$C = \frac{dQ}{dt}$$

and will depend on the particular path followed between the tempera-
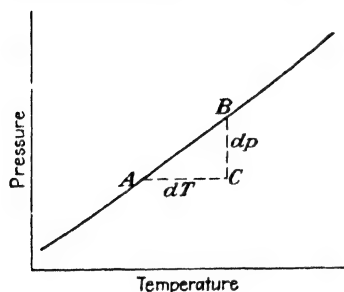
Fig. VI.17.—Specific heat of a saturated vapor.

tures. The specific heat of a saturated phase, either liquid or vapor, is the net heat effect in going from one point on the saturation line to another on the same line at an infinitesimal distance from the first, divided by the small increment of temperature. In Fig. VI.17, let A and B be two points on the vapor-pressure curve representing two states of saturated vapor differing infinitesimally in p and T. The direct path from A to B can be regarded as made up of two independent changes, one at constant pressure (path AC) and the other at constant temperature (path CB). From Eq. (III.95) we have

$$T\, dS = dQ = C_p\, dT - T\left(\frac{\partial v}{\partial T}\right)_p dp \qquad \text{(VI.60)}$$

and

$$\frac{dQ}{dT} = C_s = C_p - T\left(\frac{\partial v}{\partial T}\right)_p \frac{dp}{dT} \qquad \text{(VI.61)}$$

where dp/dT is the slope of the vapor-pressure line. This equation may be applied to either phase. It is apparent that the specific heat of saturated liquid, C'_s, is substantially the same as C_p for the liquid over the same temperature range because the coefficient $(\partial v/\partial T)_p$ is very small (excluding the region near the critical point).

Depending on the relative magnitude of the two terms on the right-hand side of Eq. (VI.61), the specific heat of saturated vapor, C''_s, may be positive, negative, or zero. In the case of steam under most circumstances it is negative. This always appears astonishing to one who is accustomed to think only of specific heats at constant pressure or at constant volume, which are always positive. That C''_s for steam is negative may readily be shown by values selected from a steam table for two saturated vapors that are close enough together so that we may assume that $\Delta p/\Delta T = dp/dT$ and similarly for the other derivatives.

Illustration 15.—Calculate the specific heat of saturated steam at 350°F. The following values were read from the Keenan-Keyes steam table:

$t_1 = 348°F.$ $p_1 = 131.17$ lb./sq. in. $v_1 = 3.426$ cu. ft./lb.
$t_2 = 352°F.$ $p_2 = 138.16$ $v_2 = 3.261$

In order to find C_p and $(\partial v/\partial T)_p$ we shall take the following two states along a constant-pressure line:

$t_3 = 344.94°F.$ $p_3 = 126.00$ $v_3 = 3.560$ $H_3 = 1,191.2$ B.t.u./lb.
$t_4 = 355.00°F.$ $p_4 = 126.00$ $v_4 = 3.619$ $H_4 = 1,197.3$ B.t.u./lb.

$$C_p = \left(\frac{\Delta H}{\Delta T}\right)_p = \frac{1,197.3 - 1,191.2}{355.00 - 344.94} = 0.606$$

$$\left(\frac{\Delta v}{\Delta T}\right) = \frac{3.619 - 3.560}{10.06} = 0.00587$$

$$\frac{\Delta p}{\Delta T} \text{ along the saturation line} = \frac{138.16 - 131.17}{4.00} = 1.748$$

From Eq. (VI.61), $C''_s = 0.606 - (350 + 459.7)(0.00587)(1.748)\left(\dfrac{1}{5.40}\right) = -0.932$

5.40 is the mechanical equivalent of heat for the units employed.

The physical interpretation of the negative specific heat is quite simple. Again in Fig. VI.17, along path AC, heat must be added and the vapor becomes slightly superheated. In order to return the vapor to the saturated state it must be isothermally compressed from C to B, and this involves a removal of heat. If the heat to be removed along CB is greater than the heat added along AC, as in the case for saturated steam under the condition chosen, the specific heat will be negative.[1]

An interesting corollary of this is the deduction of what happens when saturated steam at this condition is expanded adiabatically and reversibly. For such a case, $dQ = 0$ and $dS = 0$, and hence

$$C_p \, dT = T \left(\frac{\partial v}{\partial T}\right)_p dp$$

Now since $T(\partial v/\partial T)_p \, dp$ is greater than $C_p \, dT$ for a change from B to A, as we have just seen, or, in other words, since more heat is added along BC than is removed along CA, then, for the adiabatic change, it is clear that further heat must be removed from the steam after point A is reached, *i.e.*, it must be partially condensed. In other words, when saturated steam expands adiabatically and isentropically, it becomes wet; conversely, when it is compressed, it becomes superheated. From the above proof this statement follows strictly only for expansion or compression though an infinitesimal range of pressure, but practically it can be extended to apply to a finite range.

[1] As a matter of fact, there is nothing unique about the negative specific heat of a saturated vapor. Consider an ideal diatomic gas at 0°C. and 1 atm. that changes in state to 25°C. and 1.50 atm. One can easily show that the mean specific heats of two of the paths by which the change might take place are negative.

This type of behavior is exhibited by many other substances, typical examples being CO_2, NH_3, and O_2, and leads to a temperature-entropy diagram of the general form shown in Fig. VI.3.   Other substances— many hydrocarbons, for example—have positive specific heats of the saturated vapor, in certain regions at least, and this leads to the opposite behavior upon compression and expansion from that of steam.   A typical TS diagram for such a substance is shown in outline in Fig. VI.18. AB indicates the path of an adiabatic expansion or compression and shows that the superheated vapor becomes "wet" on compression, which is just the opposite of the behavior of steam.
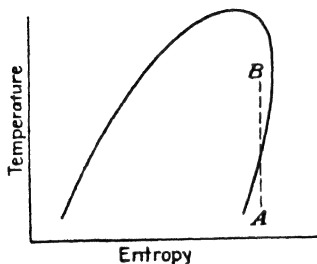
Fig. VI.18.—Outline of a temperature-entropy diagram of the hydrocarbon type.

Change of Latent Heat of Vaporization with Temperature.—From the Clausius-Clapeyron equation

$$L = T \, \Delta v \, \frac{dp}{dT}$$

the latent heat can be calculated as a function of the temperature if the vapor pressure and specific volumes of both phases are known over the whole temperature range.   Though dp/dT increases with temperature, Δv decreases at a greater rate and the net result is a decrease in latent heat with increase in temperature, the value necessarily reaching zero at the critical point where $\Delta v = 0$.

The following equations for the change of L with temperature are of interest but not of great practical importance though some of them have been used in checking the consistency of thermodynamic data. From the definition of the specific heat of a saturated phase and from the first law of thermodynamics

$$C_s = \frac{dQ}{dT} = \frac{dE}{dT} + p \, \frac{dv}{dT} \tag{VI.62}$$

Applying this to both phases and subtracting the two equations

$$C''_s - C'_s = \frac{d(E'' - E')}{dT} + p \, \frac{d(v'' - v')}{dT} \tag{VI.63}$$

Now
$$L = H'' - H' = E'' - E' + p(v'' - v') \tag{VI.64}$$

Differentiating with respect to T,

$$\frac{dL}{dT} = \frac{d(E'' - E')}{dT} + p \, \frac{d(v'' - v')}{dT} + (v'' - v') \frac{dp}{dT} \tag{VI.65}$$

From Eqs. (VI.63) and (VI.65),

$$C_s'' - C_s' = \frac{dL}{dT} - (v'' - v') \frac{dp}{dT} \tag{VI.66}$$

By the Clausius-Clapeyron equation,

$$(v'' - v') \frac{dp}{dT} = \frac{L}{T} \tag{IV.153}$$

$$\therefore C_s'' - C_s' = \frac{dL}{dT} - \frac{L}{T} \tag{VI.67}$$

Assuming $C_s' = C_p'$, Eq. (VI.67) becomes

$$C_s'' = C_p' + \frac{dL}{dT} - \frac{L}{T} \tag{VI.68}$$

Illustration 16.—Using Eq. (VI.68), calculate C_s'' for the same case as in Illustration 15, *viz.*, saturated steam at 350°F.

From the Keenan-Keyes tables,

$$t = 340°F. \qquad L = 879.0$$
$$t = 360°F. \qquad L = 862.2$$
$$\frac{\Delta L}{\Delta T} = -\frac{16.8}{20} = -0.840 \text{ B.t.u./lb./°F.}$$

At 350°F.,
$$L = 870.7 \qquad C_p' = 1.052$$
$$\therefore C_s'' = 1.052 - 0.840 - \frac{870.7}{809.7} = -0.864$$

Considering the approximate nature of the calculation, the agreement with the result obtained in Illustration 15 is reasonably good.

From Eq. (VI.67), (VI.61), and (IV.154) one can readily derive

$$\frac{dL}{dT} = \frac{L}{T} + C_p'' - C_p' - \frac{L}{v'' - v'} \left[\left(\frac{\partial v''}{\partial T} \right)_p - \left(\frac{\partial v'}{\partial T} \right)_p \right] \tag{VI.69}$$

and

$$\frac{dL}{dT} = C_p'' - C_p' + \left\{ \left[v'' - T \left(\frac{\partial v''}{\partial T} \right) \right] - \left[v' - T \left(\frac{\partial v'}{\partial T} \right) \right] \right\} \frac{dp}{dT} \tag{VI.70}$$

Equation (VI.70) can also be written

$$\frac{dL}{dT} = C_p'' - C_p' + \left[\left(\frac{\partial H''}{\partial p} \right)_\tau - \left(\frac{\partial H'}{\partial p} \right)_\tau \right] \frac{dp}{dT} \tag{VI.71}$$

in which form it was used by Sage, Evans, and Lacey[1] to calculate the latent heats of vaporization of propane and *n*-pentane. If one has data on the volumes of the saturated phases, the Clausius-Clapeyron equation is a much simpler way of calculating L than the above equation.

[1] SAGE, B. H., H. D. EVANS, and W. N. LACEY, *Ind. Eng. Chem.*, **31**, 763–767 (1939).

The general relation

$$\left(\frac{\partial \, \Delta H}{\partial T}\right)_p = \Delta C_p \qquad (\text{VI.72})$$

has sometimes been applied to the case of vaporization, but it should be recognized that this is a rigorous relationship only for the case where the pressure is constant. In the case of phase equilibrium, the pressure is a unique function of temperature and cannot be held constant. On the other hand, at moderate pressures, even for the vapor, the constant-pressure specific heat does not change much with the pressure and hence ΔC_p in the above equation can be taken, to a close approximation, to be the difference between C_p of the vapor and that of the liquid at atmospheric pressure.

If we write

$$\Delta C_p = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 \qquad (\text{VI.73})$$

where

$$\Delta\alpha = \alpha_{\text{vapor}} - \alpha_{\text{liquid}}$$

(with similar expressions for the other coefficients) and combine this with Eq. (VI.72) in the form

$$\frac{dL}{dT} = \Delta C_p \qquad (\text{VI.74})$$

and integrate between limits of T and T_B (normal boiling point), we get

$$L_T = L_B + \Delta\alpha(T - T_B) + \tfrac{1}{2} \, \Delta\beta(T^2 - T_B^2) + \tfrac{1}{3} \, \Delta\gamma(T^3 - T_B^3) \quad (\text{VI.75})$$

With this equation the latent heat of vaporization at any temperature (provided that the pressure is not too high) can be calculated from that at the normal boiling point T_B if one has data on isobaric heat capacities of the two phases.

By combining Eq. (VI.75) with Eq. (VI.46) and integrating between limits of T and T_B we get the following useful equation for interpolation and extrapolation of vapor pressure data:

$$\ln p = \frac{A}{T} + B \ln T + CT + DT^2 + E \qquad (\text{VI.76})$$

where

$$A = \frac{L_B}{R} - \frac{\Delta\alpha T_B}{R} - \frac{\Delta\beta T_B^2}{2R} - \frac{\Delta\gamma T_B^3}{3R}$$

$$B = \frac{\Delta\alpha}{R}$$

$$C = \frac{\Delta\beta}{2R}$$

$$D = \frac{\Delta\gamma}{6R}$$

$$E = \frac{L_B}{RT_B} - \frac{\Delta\alpha}{R} - \frac{\Delta\alpha}{R} \ln T_B$$

This is the same form as Eq. (VI.53), but all the constants can be calculated if one knows the specific heats of the two phases as a function of temperature, the normal boiling point, and the latent heat of vaporization at that point.

THE THERMODYNAMIC NETWORK

The ensemble of all the most important thermodynamic properties of a given fluid, particularly, v, H, E, and S, as functions of pressure and temperature has been aptly termed the "thermodynamic network." This ensemble is generally presented as a series of tables or in the form of one or more of the thermodynamic diagrams already discussed. The assembling of the complete network from a minimum of experimental measurements and the checking for consistency constitute a problem of considerable magnitude requiring much painstaking work and ingenuity. Although we cannot enter into many details, nevertheless it will be worth while to give a bird's-eye view of some of the methods that have been used in particular instances, without at all attempting to be complete in any one case.

The Keenan-Keyes steam tables, excluding for the moment the region near the critical point, are based essentially on the following data:

1. Vapor pressure of water.

2. Specific volume of water vapor throughout the entire pressure and temperature range of the network.

3. Specific heat of water vapor as a function of temperature at zero pressure as deduced from band spectra.

4. Specific volume of liquid water.

5. Latent heat of vaporization at one temperature.

6. Enthalpy of saturated liquid over the entire temperature range.

The enthalpy of the vapor was obtained by application of Eq. (VI.1), the integrations being performed algebraically with the aid of a power-series function for C_{p° and an equation of state that represented very accurately the measured volumes of superheated vapor. Saturation volumes were obtained by extrapolation of the volume data to the known saturation pressure at a given temperature, a special equation of state being used. The arbitrary integration constant was evaluated from the enthalpy at 212°F. and 1 atm. given by calorimetric measurements made at the Bureau of Standards.[1]

Entropy of the vapor was obtained in the same way as the enthalpy, using Eq. (VI.17). The integration constant was evaluated from the entropy at 1 atm. and 212°F., also obtained from the Bureau of Standards calorimetric measurements.

[1] OSBORNE, STIMSON, and FIOCK, *op. cit.*

The data on liquid volume (item 4) served to determine enthalpy and entropy for the liquid away from the saturation line, the integrations being carried out by a combination of algebraic and graphical methods. Enthalpy of saturated liquid was taken from the work of Osborne and coworkers. Entropies of liquid were obtained by subtracting entropy of vaporization from that of saturated vapor, the ΔS of vaporization being known from the ΔH.

Somewhat different methods were used to obtain the properties in the region near the critical point because the formulations developed were not satisfactory in this region where derivatives change so rapidly. The basis for the properties in this region was the enthalpy measurements of Havliček and Miškovsky, which were related to the pressure and the temperature by a semigraphical formulation. Volumes and entropies were calculated from these H values with the aid of the relations previously presented.

The properties deduced by the above methods can be checked for consistency and for agreement with related data obtained by others in several ways, of which the following are typical examples:

1. Calculated enthalpies are compared with the ones directly measured at the Bureau of Standards.
2. Specific heats can be calculated from the enthalpies by the relation

$$C_p = (\partial H / \partial T)_p$$

   and compared with direct measurements.
3. Joule-Thomson coefficients can be computed from the enthalpy equation by differentiation $[\mu = (\partial T / \partial p)_H]$ and compared with the directly measured values.
4. The Clausius-Clapeyron equation offers a test of the consistency of the following data:
   a. Vapor pressure.
   b. Specific volumes of saturated liquid and vapor.
   c. Difference in enthalpy of saturated vapor and liquid.

Illustration 17.—Some measurements of the thermodynamic properties of n-butane gave the following values at 32°C.:

Density of saturated liquid = 0.5635 g. per cc.
Density of saturated vapor = 0.00756 g. per cc.
Latent heat of vaporization = 85.2 g.-cal. per g.

The vapor pressure as a function of temperature was found to be represented by the equation

$$\log_{10} p_{atm} = a + \frac{b}{T} + 1.75 \log_{10} T + cT$$

T is in degrees Kelvin.

$$a = 1.7568 \qquad b = -1,337.8 \qquad c = -0.004070$$

With the aid of thermodynamics, show whether or not the above values are consistent.

[1] Havliček and Miškovský, *op. cit.*

Differentiating the vapor-pressure equation and substituting $T = 305.2$ give

$$\frac{dp}{dT} = 0.029462p$$

At $T = 305.2$, $p = 3.006$.

$$\therefore \frac{dp}{dT} = 0.08856$$

Using the Clausius-Clapeyron equation,

$$\frac{dp}{dT} = \frac{L}{T \, \Delta v}$$

$$= \frac{85.2 \times 41.33}{305.1 \left(\dfrac{1}{0.00756} - \dfrac{1}{0.5635} \right)}$$

$$= 0.08831$$

The agreement is within 0.3 per cent, which is good.

The thermodynamic network for propane[1] was built up from the following items of data, all measured in one laboratory:

1. Specific volume of liquid and vapor as a function of pressure and temperature.

2. Vapor pressure.

3. Specific heat of liquid as a function of pressure and temperature. In this case the slopes and integrations were all obtained graphically. The entropy of vaporization was calculated from the Clausius-Clapeyron equation.

The development of the Keenan-Keyes steam tables illustrates a case where the thermodynamic properties were essentially derived from very complete and highly accurate volume measurements all obtained in one laboratory and where there was available a wealth of other measurements to check the accuracy of the results. More often one is confronted with the problem of assembling data from a variety of sources—data that are frequently incomplete and not always consistent—and developing the thermodynamic network from them. An example of this kind is afforded by the work of Millar and Sullivan[2] on the thermodynamic properties of oxygen and nitrogen. Their method may be briefly outlined as follows:

Available data (particular reference to oxygen):

1. Specific heat C_p of liquid at 1 atm. from the normal boiling point of N_2 to that of O_2.

2. Specific heat C_p of gas at 1 atm.

3. Vapor pressure.

4. Heat of vaporization at 1 atm.

[1] SAGE, B. H., J. G. SCHAAFSMA, and W. N. LACEY, *Ind. Eng. Chem.*, **26**, 1218–1224 (1934).

[2] MILLAR and SULLIVAN, *op. cit.*

5. Density of saturated vapor.

6. Density of saturated liquid.

7. Scattered pvT data in the superheated region.

Enthalpy and entropy were taken to be zero for both liquids at the normal boiling point of nitrogen (77.4°K.).

Item 1 served to determine the H and S of liquid oxygen at its normal boiling point. H and S of saturated vapor at 1 atm. were then obtained from item 4, and these were extended into the superheated region along the constant-pressure line of 1 atm. by item 2. H and S values along other isobars in the superheated region could be obtained from item 7. The values on the saturated-vapor line were determined from the saturated volumes, which were obtained by extrapolation of the isometrics for the superheated vapor to the known vapor-pressure curve. H and S of saturated liquid could then be obtained by subtracting latent heats of vaporization from the corresponding values for saturated vapor, the latent heats having been obtained from the Clausius-Clapeyron equation using data of items 3, 5, and 6.

Smoothing of data and determination of slopes and integrals were, for the most part, done graphically. To prepare the thermodynamic diagrams, plots were made of H vs. T at constant p, H vs. p at constant T, and p vs. T at constant H and adjustments made to secure smooth curves on all three charts and to obtain reasonable variations of C_p (slope of the isobars on the HT chart) with temperature. A TS chart was then prepared in a similar manner, the constant p lines being located from those on the HT chart by graphical integration of the equation

$$dS = \frac{dH}{T} \qquad \text{(constant pressure)}$$

The final results of all these calculations were incorporated into $\log p$ vs. H diagrams and tabulations of properties.

CHAPTER VII

COMPRESSION AND EXPANSION OF FLUIDS

In many chemical processes, fluids undergo changes of pressure, and it is important for the chemical engineer to be able to relate such changes to the changes in other state variables and to the accompanying energy effects. Especially within the last decade or two, pressure has become of the greatest importance as a variable with which to influence the course of a chemical reaction or a physical change. Every year witnesses the development of one or more new processes in which pressure effects are of primary importance and in which expansion and/or compression of fluids takes place. It is the purpose of this chapter to develop and illustrate by application to specific problems the quantitative relationships governing the various types of compression or expansion that fluids may undergo, in order to enable the engineer to answer questions of which the following are typical:

1. How much work is required to compress a gas from one pressure to another?
2. How is the amount of work affected by such factors as

    a. Type of compression cycle?
    b. Initial temperature?
    c. Nature of the gas?

3. How much heat must be removed in the compression, or what temperature will be attained if no heat is removed?
4. When is it advantageous to compress a gas in more than one stage?
5. How does the state of a gas or vapor change when it is expanded through a throttle?

COMPRESSION EQUIPMENT—GENERAL DESCRIPTION AND CLASSIFICATION

Throughout this book, descriptions of equipment have been avoided as far as possible, but a few general remarks on equipment for the compression of gases seem desirable as a foundation for the better understanding of the quantitative treatment.

Any machine that increases the pressure of a gas might reasonably be called a "compressor," but the term is generally restricted to certain classes of machines, especially those operating at pressures above a few atmospheres. The pressures commonly dealt with in industry may range all the way from a high vacuum to 15,000 lb. per sq. in. A machine the intake pressure of which is well below that of the atmosphere and

which discharges gas at substantially atmospheric pressure is generally known either as a "vacuum pump" or as "an exhauster." Such machines do not differ in principle from those which take in gas at atmospheric pressure and discharge it at a higher pressure, and we shall make no distinction between them in our discussion of principles.

Partly on the basis of the pressure range over which they operate and partly on the basis of operating principle, compressing devices may be roughly classified as (1) centrifugal fans; (2) rotary, or positive-pressure, blowers; (3) centrifugal compressors, or turbocompressors; (4) piston, or reciprocating, compressors; and (5) jet compressors. Centrifugal fans operate on the principle of imparting a high velocity to the gas and then allowing the kinetic energy due to the velocity to do work in compressing the gas. They are generally limited to pressure differences between intake and exhaust of about 0.5 lb. per sq. in. (approximately 1 ft. of water).

The pressure range from 0.5 lb. to about 50 lb. per sq. in. is served by rotary machines that produce pressure by volume displacement rather than by imparting high velocity.

Centrifugal compressors are the same in principle as centrifugal fans but are sturdier and operate at higher speeds, thus allowing higher pressures—up to 15 lb. per sq. in. in a single stage—to be attained. By coupling together on a single shaft two or more individual stages, with diffusing vanes between for conversion of the kinetic energy, still higher pressures can be secured; multistage machines of this type have been built for pressures up to 175 lb. per sq. in. Such a multistage centrifugal compressor is similar to a steam turbine both in principle and in general construction. The pressure per stage depends on the size and speed of rotation; in general, the maximum pressure ratio per stage is about 1.2. As many as 30 stages have been used. The advantages of this type of compressor as compared with piston compressors are (1) compactness, (2) no valves, (3) no large wearing parts, (4) freedom from pulsation of the discharged gas, (5) simpler regulation of the volume, (6) low maintenance, and (7) the fact that it can be direct-connected to a turbine.

The jet compressor differs from all others in having no moving parts. The kinetic energy of a high-velocity jet of one fluid is used to do work on and therefore compresses another fluid. The jet fluid most commonly used is steam.

By far the most important machine for pressures above 50 lb. per sq. in. and the one with which we shall be mainly concerned in this chapter is the piston compressor, a diagrammatic representation of which is given in Fig. VII.1. Its essential features are the cylinder A, piston and piston rod B, intake and discharge valves C and D, respectively, and the water jacket E (note, however, that some compressors are air-

cooled). If compression occurs only on one side of the piston, the compressor is known as a "single-acting" one; if on both sides, it is said to be "double acting." Further classification of reciprocating compressors may be made as follows:

1. Single-stage, two-stage, or multistage. A single-stage compressor is one in which the whole range of compression from intake to final pressure is accomplished in one cylinder, *i.e.*, in one step or stage. In two- and multistage machines there are two or more cylinders in series, each compressing over only a part of the total pressure range. Between cylinders (*i.e.*, stages) the gas is cooled by means of water or air in an intercooler.
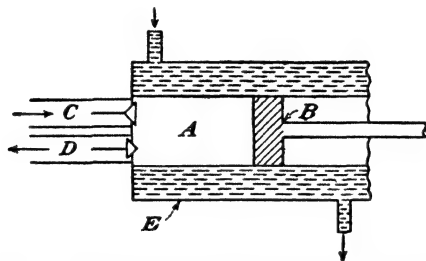
Fig. VII.1.—Diagram of a simple reciprocating compressor.

2. Vertical, horizontal, or angle. This refers to whether the axis of the cylinder is vertical or horizontal or whether both arrangements are used in a given compressor.

3. Power-driven, steam-driven, or gas-driven. The power-driven compressor is one driven by an electric motor either through a belt or through a chain or when direct connected to the motor shaft. A steam-driven compressor is one actuated by a steam engine of the reciprocating type with a direct connection between the piston of the compressor and that of the steam engine. The steam engine may be either simple (*i.e.*, steam expanded in one step or stage) or compound (steam expanded in more than one stage). A gas-driven compressor is one in which the motive power is supplied by an internal-combustion engine using gas as fuel.

4. Straight-line or duplex. In a straight-line compressor all the cylinders, whether for the gas being compressed or for delivering the motive power, are arranged horizontally with a common axis. A duplex machine is one having two parallel sets of compressing units arranged side by side and driven from a common crankshaft.

An expander is simply the reverse of a compressor in that it takes in gas at high pressure and expands it to a lower pressure with delivery of a certain amount of work. A steam engine, whether of the turbine or of the reciprocating type, is an expander used primarily to obtain power.

An expander in the sense that is meant in this book is an engine either of the turbo or of the reciprocating type used primarily for the purpose of producing refrigeration.

Most of the treatment in the remainder of this chapter will refer specifically to the reciprocating compressor. The theory of the centrifugal compressor, while similar in many respects, differs in some important particulars and is outside the scope of this book. For further information on this type of compressor, the reader is referred to the book by Kearton.[1]

CHANGES OF STATE OF GASES

Fundamental Equations.—The differential equations for changes of state of any fluid in terms of the common independent variables were derived from the two laws of thermodynamics in Chap. III; three of them are assembled here for ready reference:

$$dQ = T \, dS = C_v \, dT + T \left(\frac{\partial p}{\partial T} \right)_v dv \qquad \text{(III.88)}$$

$$dQ = T \, dS = C_p \, dT - T \left(\frac{\partial v}{\partial T} \right)_p dp \qquad \text{(III.95)}$$

$$dQ = T \, dS = C_p \left(\frac{\partial T}{\partial v} \right)_p dv + C_v \left(\frac{\partial T}{\partial p} \right)_v dp \qquad \text{(III.103)}$$

These equations are quite general and apply to any fluid and any kind of change of state in a homogeneous system in which only mechanical forces are involved. If these equations are interpreted as dealing only with the internal properties of the system itself, then the question of reversibility does not enter. This question does enter, however, when one considers the reaction between the system and its surroundings. If we stipulate that the change is reversible in relation to its environment, then we may write

$$T \, dS = dQ$$

From the first law, $\qquad dQ = dE + dW$

and again, if the process is reversible,

$$dW = p \, dv$$

Let it be emphasized again that heat and work are not properties but the external effects of the interaction of the system and the surroundings. When the forces (used in the general sense of any driving force) are balanced, we have a reversible process, and this is the only case for which we can calculate the heat and work effects solely from the properties of the system. This is, of course, an ideal situation, which is not

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[1] KEARTON, W. J., "Turbo-blowers and Compressors," Sir Isaac Pitman & Sons, Ltd., London, 1926.

reached in practice but can be approached as a limit. In all actual changes there will be irreversible effects due to mechanical friction, fluid friction, temperature differences, and the like; consequently, the actual heat and work will differ from the ideal heat and work by an indeterminate amount. The ideal quantities that we calculate are useful as standards of performance and also as approximations of the actual quantities, and they can be converted to actual quantities by certain factors, generally called "efficiencies," that must be determined by measurement. To avoid confusion we shall, in some cases, use the term "theoretical work" to denote the ideal reversible work calculated from the properties and the term "actual work" to denote the estimated work in a practical device after allowance for irreversible effects.

For the special case where the fluid in question may be regarded as an ideal gas the differential coefficients of the general equations are readily evaluated from the equation of state

$$pv = RT \qquad \text{(per mole)}$$

and these equations reduce to (see Chap. III, page 100),

$$T \, dS = dQ = C_v \, dT + p \, dv \qquad \text{(VII.1)}$$

$$T \, dS = dQ = C_p \, dT - RT \frac{dp}{p} \qquad \text{(VII.2)}$$

$$T \, dS = dQ = C_p T \frac{dv}{v} + C_v T \frac{dp}{p} \qquad \text{(VII.3)}$$

Constant-pressure Change.—For this special case it follows at once that

$$Q = \int_{T_1}^{T_2} C_p \, dT$$

and
$$W = \int_{v_1}^{v_2} p \, dv = p(v_2 - v_1) \qquad \text{(VII.4)}$$

v_1 and v_2 are the two specific (or molal) volumes at the beginning and end of the change of state. An equation of the same form, *viz.*,

$$W = p(V_2 - V_1) \qquad \text{(VII.5)}$$

will be used for another constant-pressure process in which no change of state is involved and for which the work is merely the mechanical work of injection (or ejection) of a fluid into a space maintained at constant pressure. This is a term that comes into consideration in many cyclic or continuous-flow processes. The two volumes V_1 and V_2 are not two different states but merely the two limits of a displacement. Note that the pressure in both equations is absolute and not gauge pressure.

Constant-temperature, or Isothermal, Change.—For an ideal gas,

$$W = \int_{v_1}^{v_2} p \, dv = RT \int_{v_1}^{v_2} \frac{dv}{v} = -RT \int_{p_1}^{p_2} \frac{dp}{p}$$

or $$W = -RT \ln \frac{p_2}{p_1} = -2.3026RT \log \frac{p_2}{p_1} \quad \text{(per mole)} \quad \text{(VII.6)}$$

This expression holds for either compression or expansion between the given pressure limits. For compression, $p_2 > p_1$, and the work is negative (work done on the system). For expansion, $p_1 > p_2$, and the work is positive. By Eq. (VII.1) or (VII.2),

$$dQ = dW$$

(this also follows from one of the definitions of the ideal gas, *viz.*, that $dE = 0$ at constant T). Thus we see that when an ideal gas is compressed isothermally an amount of heat equivalent to the work must be removed from the gas. In other words, all the work done is dissipated as heat to the surroundings; none of it is stored up in the compressed gas. At first thought this might seem like a very wasteful and inefficient process. Actually, this is not so, because all the work (theoretically) can be recovered by allowing the gas to expand and maintaining its temperature constant by an influx of the same quantity of heat previously transferred to the surroundings.

For a nonideal gas, the isothermal work can be obtained in a variety of ways. If the compressibility data are available, a pv curve can be plotted, and the work is obtained graphically as the area under the pv curve down to the $p = 0$ axis.

If an equation of state is available, the heat of compression may be obtained by integration of Eq. (III.88) or (III.95) and the work by integration of $p\, dv$. Thus, if the gas obeys the van der Waals' equation,

$$dQ = T \left(\frac{\partial p}{\partial T} \right)_v dv$$

$$= RT \frac{dv}{v - b}$$

$$Q = RT \int_{v_1}^{v_2} \frac{dv}{v - b}$$

$$= RT \ln \frac{v_2 - b}{v_1 - b} \quad \text{(VII.7)}$$

and $$W = \int_{v_1}^{v_2} p\, dv$$

$$= RT \int_{v_1}^{v_2} \frac{dv}{v - b} - a \int_{v_1}^{v_2} \frac{dv}{v^2}$$

$$= RT \ln \frac{v_2 - b}{v_1 - b} - a \left(\frac{1}{v_1} - \frac{1}{v_2} \right) \quad \text{(VII.8)}$$

and similarly for other equations of state.

If a temperature-entropy diagram of the fluid in question is available, the heat and work are obtained as follows: From the definition of entropy,

$$Q = T \, \Delta S \qquad \text{(reversible process)}$$

where ΔS is the difference in entropy between the two points of intersection of the given isotherm with the two constant-pressure lines representing the limits of the compression or expansion. By the first law,

$$
\begin{aligned}
W &= Q - \Delta E \\
&= T \, \Delta S - \Delta E \\
&= -\Delta A \qquad\qquad\qquad \text{(VII.9)}
\end{aligned}
$$

Values of the function A are not generally tabulated or plotted on thermodynamic diagrams, but the work can be obtained by subtracting ΔE from $T \, \Delta S$, ΔE in turn being obtained from ΔH and $\Delta \, pv$.

In the case of a gas that is far from ideal the difference between the heat and the work may be very appreciable though for many practical purposes they can usually be assumed equal.

Illustration 1.—Calculate (a) the theoretical work required to compress isothermally 1 lb.-mole of CO_2 initially at 70°F. and 1 atm. to 500 lb. per sq. in. abs. and (b) the heat to be removed, for three cases: (1) if CO_2 is assumed ideal, (2) if the van der Waals' equation is assumed, and (3) using actual properties as given on a TS diagram.

$$
\begin{aligned}
W &= -2.3026RT \log \frac{p_2}{p_1} \\
&= -4.571 \times 530 \log \frac{500}{14.7} = -3,720 \text{ B.t.u.} \\
&= \frac{-3,720 \times 778}{33,000 \times 60} \text{ hp.-hr.} \\
&= -1.46 \text{ hp.-hr.} \\
Q &= W = -3,720 \text{ B.t.u.}
\end{aligned}
$$

2. From Table IV in the Appendix,

$$
\begin{aligned}
a &= 925 \text{ (atm.)(cu. ft.)}^2 \\
b &= 0.686 \text{ cu. ft.}
\end{aligned}
$$

v_1 (from the ideal-gas equation) $= 387$ cu. ft.

v_2 (from the van der Waals' equation by trial) $= 9.40$ cu. ft.

Substituting in Eq. (VII.8),

$$
\begin{aligned}
W &= 4.571 \times 530 \log \frac{9.40 - 0.69}{387 - 0.7} - 925 \left(\frac{1}{387} - \frac{1}{9.40} \right) \times 2.72^* \\
&= -3,996 + 261 = -3,735 \text{ B.t.u.}
\end{aligned}
$$

By Eq. (VII.7),

$$Q = -3,996 \text{ B.t.u.}$$

* 1 cu. ft. atm. = 2.72 B.t.u.

3. From the TS chart,[1]

$$S_1 = 1.417, \qquad S_2 = 1.232 \text{ (B.t.u./lb./°R.)}$$
$$H_1 = 312, \qquad H_2 = 294.5 \text{ (B.t.u./lb.)}$$
$$v_1 = 8.5 \text{ cu. ft./lb.} = 374 \text{ cu. ft./lb.-mole}$$
$$v_2 = 0.215 \text{ cu. ft./lb.} = 9.46 \text{ cu. ft./lb.-mole}$$

$$\Delta E \text{ (per mole)} = 44 \left[(H_2 - H_1) - \frac{p_2v_2 - p_1v_1}{J} \right] = -629 \text{ B.t.u./lb.-mole}$$

By Eq. (VII.9),

$$W = 530(1.232 - 1.417)44 + 629 = -3,686 \text{ B.t.u.}$$
$$Q = T \, \Delta S = -4,315 \text{ B.t.u.}$$

The difference between the heat and work is 17 per cent of the work; and it is of interest to note that, at the higher pressure, the volume of CO_2 deviates about 20 per cent from that of an ideal gas.

The isothermal work is the absolute minimum amount of work that must be used to compress a gas over a given pressure range (or, conversely, the maximum work that could be secured by expanding the gas over the same range). In practice, isothermal compression is not realized because it is not practicable to remove the heat of compression rapidly enough. In fact, in actual compressors only a relatively small percentage of the heat is removed, and the compression more nearly approaches the other limiting case, *viz.*, adiabatic compression.

Adiabatic Change.—For a reversible adiabatic change of state,

$$T \, dS = dQ = 0 \tag{VII.10}$$

For an ideal gas, by Eqs. (VII.3) and (VII.10),

$$C_p \frac{dv}{v} + C_v \frac{dp}{p} = 0 \tag{VII.11}$$

or

$$\frac{C_p}{C_v} \frac{dv}{v} + \frac{dp}{p} = 0 \tag{VII.12}$$

Integrating on the assumption that C_p/C_v is a constant,

$$k \ln v + \ln p = K \quad \text{(constant of integration)} \tag{VII.13}$$

or

$$pv^k = K_1 \tag{VII.14}$$

and

$$pv^k = p_1v_1^k = p_2v_2^k = \cdots \tag{VII.15}$$

where $k = C_p/C_v$.

The corresponding equations in p, T and v, T can be obtained by integration of Eqs. (VII.2) and (VII.1), respectively, or more simply by combining Eq. (VII.14) and the ideal-gas equation. The resulting

[1] PLANK, R., and J. KUPRIANOFF, *Beihefte zur Z. ges. Kälte Ind.*, **1**, 9–65 (1929).

A smaller diagram in English units, transposed by F. B. Hunt from the data of Plank and Kuprianoff, was published in 1930 by the Liquid Carbonic Corporation of Chicago, Ill., and is reproduced in the Appendix.

equations are

$$Tv^{k-1} = K_2 \tag{VII.16}$$

$$Tp^{\frac{1-k}{k}} = K_3 \tag{VII.17}$$

Equations (VII.14), (VII.16), and (VII.17) relate the changes in the state variables that accompany a *reversible* adiabatic expansion or compression of an ideal gas. They are not exact even for the ideal gas because the specific-heat ratio k is not a constant though the variation in k is not great over the relatively narrow range usually encountered.

Substituting in the general expression for work the value of p as given by Eq. (VII.15),

$$W = p_1 v_1^k \int_{v_1}^{v_2} \frac{dv}{v^k} \tag{VII.18}$$

$$W = \frac{p_1 v_1^k}{1-k} (v_2^{1-k} - v_1^{1-k})$$

$$W = \frac{p_1 v_1 - p_2 v_2}{k-1} \tag{VII.19}$$

Since v_2 is unknown, eliminate it by

$$v_2 = v_1 \left(\frac{p_1}{p_2}\right)^{\frac{1}{k}} \tag{VII.20}$$

Then

$$W = \frac{p_1 v_1}{k-1} \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} \right] \tag{VII.21}$$

$$W = \frac{RT_1}{k-1} \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} \right] \tag{VII.22}$$

Equations (VII.21) and (VII.22) give the theoretical adiabatic work per mole for either compression or expansion, when p_1 always refers to the *initial* pressure for either process. k is assumed to be a constant, independent of the conditions in a given case, but it does vary with the atomic complexity of the gas. A few typical values of k for ordinary temperature and pressure are as follows:

Monatomic gases (He, A, etc.)................. 1.67
Diatomic gases (H_2, CO, N_2).................. 1.40 (approximate)
Tri-, tetra-, and pentatomic (CO_2, CH_4, etc.)..... 1.30 (approximate)

Still lower values are obtained for gases of greater atomic complexity. In general, k decreases as the temperature increases and increases with pressure so that it is reasonable to assume that it remains substantially constant in an adiabatic change. The following tabulation of calculated values of k for air will give some idea of the extent of variation in k that might be expected:

t, °F.	Pounds per square inch absolute			
	0	1000	2000	4000
0	1.40	1.58		
200	1.39	1.47	1.53	1.62
400	1.38	1.43	1.46	1.51
600	1.37	1.39	1.42	1.45

Edmister[1] computed values of k for 17 hydrocarbons from C_p data at 1 atm. and a reduced equation of state and presented the results in a graph as a function of reduced pressure and temperature. In the case of pure gases for which no data on k are available or for gas mixtures it is suggested that k be calculated from the relation

$$k = \frac{C_p}{C_p - R}$$

where C_p is for one mole and R is 1.987 when the usual thermal units are used. C_p for a gas mixture may be calculated with sufficient accuracy by taking an arithmetic molal average.

Note that for a given weight of gas to be compressed the work depends only on the pressure ratio and not on the absolute pressure. In other words, the work per mole is the same for compression from 100 to 1,000 atm. as from 0.1 to 1.0 atm.

In an adiabatic compression all the work appears as energy in the compressed gas; this means that its temperature must rise (since E is independent of pressure). The temperature rise (or fall in an expansion) can be obtained from Eq. (VII.17) in the form

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} \tag{VII.23}$$

A graphical solution of this equation for a given T_1 is presented in Fig. VII.2.

Expressions for the adiabatic work could be obtained from the use of other equations of state, but they are complex and not of any practical importance. Since the actual compression work in any practical case is always greater than the ideal owing to irreversible effects that cannot be definitely determined, there may be little point in using a more exact pvT relation in the great majority of cases.

Some attempts have been made to allow for certain irreversible effects or for the fact that the process is not strictly adiabatic by assum-

[1] EDMISTER, W. C., *Ind. Eng. Chem.*, **32**, 373 (1940).

ing that the actual change of state of the gas can be represented by the equation[1]

$$pv^n = \text{constant} \tag{VII.24}$$

where n is a constant to be determined from the actual behavior of the gas in a compressor (from an indicator card, for example). Using this relation, Eqs. (VII.21) to (VII.23) would be unchanged except for the substitution of n for k. If the compression is adiabatic but accompanied by internal irreversible effects, n will be greater than k. If reversible but nonadiabatic, n will be less than k and will lie between k and 1 as limits (1 for isothermal or completely non-adiabatic compression).

In view of the fact that the difference between the work of isothermal compression and of adiabatic compression is not very great, that actual compressions are not far from adiabatic (in spite of the cooling water jacket around the cylinder), and that the calculated work is only an approximation to the actual in any case, the use of exponent n in place of k scarcely seems justified in the great majority of cases.

For the nonideal gas case, either the work or the final temperature is very simply obtained from a thermodynamic diagram. Since a reversible adiabatic compression is at constant entropy, it is necessary only

FIG. VII.2.—Temperature of adiabatic compression from an initial temperature of 70°F. p_2/p_1 = compression ratio, k = specific heat ratio.

to proceed vertically on a TS diagram from the initial to the final pressure. Since, for an adiabatic process,

$$W = -\Delta E = -\Delta H + \Delta pv$$

the work is obtained from quantities read directly from the diagram if it contains constant-volume lines. If not, the volume must be obtained independently, for example, from tables of thermodynamic properties.

[1] Such a change of state is sometimes called a "polytropic" change.

WORK OF SINGLE-STAGE COMPRESSORS

Ideal Cycle.—Up to this point we have been considering the work effects accompanying certain changes of state. Actually these changes of state form only one step of the cycle of changes that a gas undergoes in an actual continuous compression (or expansion) process. In Fig. VII.3 are represented on a pV diagram the changes that occur in the cylinder of an ideal reciprocating compressor. The changes in actual compressors are somewhat different, as will be shown later (page 288), but the use of an idealized cycle for purposes of analysis is justified on the grounds of simplicity and the fact that the results deduced from it approach the actual case closely enough for most purposes.

This diagram assumes that, when the piston has gone to the end of

FIG. VII.3.—Pressure-volume changes in an ideal single-stage compressor.

its stroke after compressing the sample of gas, there is no gas left in the cylinder between the piston and the seat of the discharge valve. This is referred to as an "assumption of no clearance." Let us assume that the piston is now ready to move back and draw in a fresh charge of gas; in other words, we start at point A on the diagram of Fig. VII.3. p_1 is the intake, or suction, pressure and is the same in the reversible case whether it refers to the pressure in the cylinder itself or in the pipe leading to the intake valve. As the piston moves to the right, the intake valve is assumed to open instantly and gas is drawn in at the constant pressure p_1 (line AB) until, at the end of the stroke, the total volume V_1 has been taken into the cylinder. As the piston starts to move back to the left, the intake valve closes and the gas is compressed, its pV changes being represented by line BC or BE as the case may be. When the pressure reaches the value p_2, which is the pressure in the discharge line from the compressor, the discharge valve opens automatically and gas is pushed from the cylinder at constant pressure until the point of zero volume, D, is reached. Since A and D are both points of zero volume, the difference in pressure is of no significance and we can imagine the change from D to A to occur instantly and then the system is ready for the cycle to be repeated.

Cycle Work.—The total work for the cycle is the sum of the individual work terms for the four steps as follows:

$$W_{cycle} = W_{AB} + W_{BC} + W_{CD} + W_{DA} \qquad \text{(VII.25)}$$

$$W_{AB} = p_1 V_1$$

$$W_{BC} = \int_{V_1}^{V_2} p \, dV$$

$$W_{CD} = -p_2 V_2$$

$$W_{DA} = 0 \qquad \text{(constant-volume process)}$$

$$\therefore W_{cycle} = p_1 V_1 - p_2 V_2 + \int_{V_1}^{V_2} p \, dV \qquad \text{(VII.26)}$$

From the calculus,

$$\int_{V_1}^{V_2} p \, dV + p_1 V_1 - p_2 V_2 = -\int_{p_1}^{p_2} V \, dp \qquad \text{(VII.27)}$$

$$\therefore W_{cycle} = -\int_{p_1}^{p_2} V \, dp \qquad \text{(VII.28)}$$

This can be evaluated algebraically or graphically. It was shown in Chap. I that the area enclosed by the pV diagram (areas $ABCD$ or $ABED$) gives the cycle work directly. In this way the engineer obtains the actual work done in a cylinder from a diagram (indicator card) automatically drawn by a mechanism attached to the compressor or expander.

Isothermal Case.—The third term of the right-hand member of Eq. (VII.26) is the work of the compression (or expansion) stroke itself and has already been evaluated for a number of specific cases. Thus, if the compression is isothermal and the gas ideal, the work of this stroke is given by Eq. (VII.6); and since $p_1 V_1 = p_2 V_2$ for an ideal gas at constant temperature and mass, Eq. (VII.6) also gives the cycle work per mole of gas handled.

For the nonideal gas we may proceed as follows:
By Eq. (III.140),

$$RT \ln \frac{f_2}{f_1} = \int_{p_1}^{p_2} v \, dp = \frac{1}{N} \int_{p_1}^{p_2} V \, dp$$

where N = number of moles.

$$\therefore W_{cycle} = NRT \ln \frac{f_1}{f_2} \qquad \text{(VII.29)}$$

Thus, for the nonideal gas, the isothermal cycle work is readily calculated if the fugacities are known. Also, since at constant temperature

$$dF = v \, dp$$

$$\text{Cycle } W(\text{per mole}) = \Delta F = F_2 - F_1$$

ΔF being taken along the isotherm. Values of F are not commonly plotted on the usual thermodynamic diagrams; but since $F = H - TS$, we can write

$$W = H_2 - H_1 - T(S_2 - S_1) \qquad \text{(VII.30)}$$

and the molal work is obtained directly from values read from a TS or similar diagram.

Adiabatic Case.—Since the temperature rises in adiabatic compression, the volume at a given pressure will be greater than for isothermal compression and the adiabatic compression stroke would be represented by a line such as BE in Fig. VII.3. It can be readily seen that the adiabatic work for a given quantity of gas and given pressure limits is somewhat greater than the isothermal work, the difference being given graphically by the area BEC.

For an ideal gas and with the additional assumption of constant k, the adiabatic-cycle work is given by substituting Eq. (VII.21) into (VII.26) and utilizing the fact that

$$p_1 V_1 - p_2 V_2 = p_1 V_1 \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]$$

which results from Eqs. (VII.19) and (VII.21).[1]
Thus we obtain

$$W_{\text{cycle}} = \frac{k p_1 V_1}{k-1} \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right] \tag{VII.31}$$

$$W_{\text{cycle}} = \frac{k N R T_1}{k-1} \left[1 - \left(\frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right] \tag{VII.32}$$

From Eqs. (VII.19) and (VII.26) we may also obtain

$$W_{\text{cycle}} = \frac{k}{k-1} (p_1 V_1 - p_2 V_2) \tag{VII.33}$$

$$W_{\text{cycle}} = \frac{k}{k-1} N R (T_1 - T_2) \tag{VII.34}$$

forms of Eq. (VII.31) that are useful in special cases. In Eq. (VII.31), V_1 is the cylinder displacement or the volume taken in per cycle in a single-acting cylinder. If n_0 is the number of cycles per minute, the total volume displaced per minute $= n_0 V_1$. If this is used for V_1 in Eq. (VII.31), we get the cycle work in power units, *i.e.*, work per unit of time. If the cylinder is double acting, the work for one cycle is twice that given by Eq. (VII.31) if V_1 is the displacement volume because there are two displacements per cycle.

Adiabatic cycle work is very easily obtained from a thermodynamic diagram as follows:

---

[1] Equations (VII.19) to (VII.21) are written for molal volume, but equations of the same form apply for total volume.

From Eq. (VII.26) and the first law,

$$W_{\text{cycle}} \text{ (per lb.)} = p_1 v_1 - p_2 v_2 - (E_2 - E_1) \qquad \text{(VII.35)}$$
$$W_{\text{cycle}} \text{ (per lb.)} = (E_1 + p_1 v_1) - (E_2 + p_2 v_2) \qquad \text{(VII.36)}$$
$$W_{\text{cycle}} \text{ (per lb.)} = -\Delta H \qquad \text{(VII.37)}$$

It is therefore necessary only to read from the diagram the values of H at the two ends of the isentropic (constant-entropy) line running between the two pressure limits. The use of a TS or similar chart is particularly desirable in those cases where the compression or expansion involves a passage through the two-phase region. In such a case (compression of a "wet" vapor, for example) the ideal-gas law or any other equation of state would be grossly in error.

Illustration 2.—Calculate the theoretical horsepower required to compress 100 cu. ft. of CO_2 per minute at $-60°F$. and 14.7 lb. per sq. in. absolute pressure to 147 lb. per sq. in. abs. Assume ideal (*i.e.*, reversible and no clearance) single-stage compressor and adiabatic compression.

Assuming ideal gas and a constant ratio of specific heats of 1.30, the power is given by substitution in Eq. (VII.31),

$$\text{Cycle work per min.} = \frac{1.30 \times 14.7 \times 144 \times 100}{0.30}\left[1 - \left(\frac{147}{14.7}\right)^{0.231}\right]$$
$$= -644,000 \text{ ft.-lb./min.}$$

$$\text{Hp.} = -\frac{644,000}{33,000} = -19.5$$

It is of interest to note that, in this case, isothermal compression would have no practical meaning because the discharge pressure is above the vapor pressure at the given temperature and therefore the CO_2 would be completely condensed to a liquid in the cylinder and then would have to be compressed as a liquid to the final pressure.

Let us now calculate the power required by means of a TS diagram for CO_2 (see Appendix) and compare it with the value based on the assumption of an ideal gas.

From the TS chart for CO_2, $\qquad H_1 = 286$ B.t.u./lb.
$$H_2 = 340 \text{ B.t.u./lb.}$$

v_1 (from the chart) $= 6.9$ cu. ft./lb.

$$\therefore \text{Hp. for adiabatic compression} = -(340 - 286) \times \frac{100}{6.9} \times \frac{778}{33,000} = -18.5$$

Since the pressure ratio is usually less than 10 in single-stage compression, we may infer from this calculation that the assumption of ideal gases usually gives sufficiently accurate results for all practical purposes, in the case of a single-stage compressor with intake pressure near atmospheric.

Illustration 3.—What would be the final temperature of the gas in the cylinder at the end of the adiabatic compression in Illustration 2?

By Eq. (VII.23), $\qquad T_2 = 400(10)^{0.231} = 680°R. = 220°F.$
By the TS diagram, $\qquad\qquad\qquad t = 214°F.$

Illustration 4.—What is the minimum work, expressed in kilowatt-hours per pound of steam, to compress adiabatically saturated steam at 300 lb. per sq. in. abs. to a pressure of 1,200 lb. per sq. in. in a continuous process?

This is a case where the use of a thermodynamic diagram is practically essential. Not only would the ideal-gas law be seriously in error, but one would not know what value to take for k.

From the Keenan-Keyes tables, $t_1 = 417.3°F.$, $H_1 = 1,202.8$ B.t.u. per lb., $S_1 = 1.5104$.

For the same value of S at 1,200 lb. per sq. in.,

$$H_2 = 1,341.8, \qquad t_2 = 743°F.$$
$$W = -\Delta H = -139.0 \text{ B.t.u./lb.}$$
$$= -\frac{139}{3,410} = -0.0407 \text{ kw.-hr.}$$

In the case of gases for which the thermodynamic properties are not available, one can calculate them from an equation of state or from generalized properties if the critical constants are known, by the methods outlined in the preceding chapter. For a gas mixture that is not ideal the simplest procedure is to calculate the pseudocritical constants according to the method of Kay and then proceed with the use of generalized properties as for a single component. For further details on such calculations, reference may be made to a paper by York.[1]

Effect of Clearance.—Obviously there must be, in any practical case, some gas volume remaining in the cylinder at the end of the discharge stroke. When the piston moves back, this high-pressure gas reexpands behind the piston and the intake valve does not open until the pressure of this gas has fallen to the value of the pressure in the intake
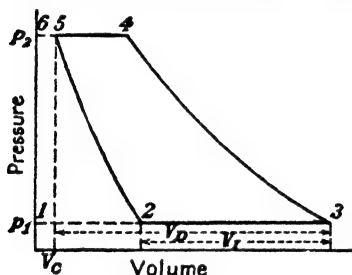
FIG. VII.4.—Pressure-volume changes in a compressor with clearance. V_D = displacement volume, V_c = clearance volume, V_I = intake volume.

manifold. The volume remaining in the cylinder between the end of the piston and the end of the cylinder and including any other volume in which gas is trapped when the valves close is known as the "clearance volume" V_c. The ratio V_c/V_D of this volume to the displacement volume, or volume swept through by the piston, is known as the "clearance." Depending on the size and design of the compressor, clearances may vary from 2 to 10 per cent.

The pV changes in a compressor with clearance may be represented by the idealized indicator diagram shown in Fig. VII.4. 3-4 is the compression stroke, 4-5 the discharge stroke, 5-2 the reexpansion stroke, and 2-3 the intake, or suction, stroke. The volume at 5 is the clearance volume V_c, $V_3 - V_5$ is the displacement volume V_D, and $V_3 - V_2$ is the volume of charge taken into the cylinder V_I. Assuming ideal gas and

[1] York, R., *Ind. Eng. Chem.*, **34**, 535-544 (1942).

constant k and that both the compression and the expansion are adiabatic and reversible, we can readily arrive at an expression for the cycle work by summing the work terms for the individual strokes.   A simpler method, however, is to note that the area 2-3-4-5 is merely the difference of the two areas 1-3-4-6 and 1-2-5-6, each of which represents a cycle of the no-clearance type for which the work is given by Eq. (VII.31).

Subtracting the work terms for these two cycles,

$$W \text{ for cycle 2-3-4-5} = \frac{kp_1V_I}{k-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} \right] \qquad \text{(VII.38)}$$

In other words, the clearance has no effect on the work provided that one uses the actual volume of gas taken in for the V_1 in Eq. (VII.31) instead of the displacement volume.

Since $V_2 = V_5(p_2/p_1)^{\frac{1}{k}}$ by Eq. (VII.20), then

$$V_3 - V_2 = V_3 - V_5\left(\frac{p_2}{p_1}\right)^{\frac{1}{k}}$$

And since
$$\frac{V_3 - V_2}{V_3 - V_5} = \frac{V_I}{V_D}$$

we have
$$\frac{V_I}{V_D} = \frac{V_3}{V_3 - V_5} - \frac{V_5}{V_3 - V_5}\left(\frac{p_2}{p_1}\right)^{\frac{1}{k}}$$

Denoting clearance by c,
$$c = \frac{V_5}{V_3 - V_5}$$

$$1 + c = \frac{V_3}{V_3 - V_5}$$

and we have
$$V_I = V_D\left[1 + c - c\left(\frac{p_2}{p_1}\right)^{\frac{1}{k}} \right] \qquad \text{(VII.39)}$$

a relation from which the theoretical intake volume V_I can be calculated from the pressure ratio, the dimensions of the cylinder, and the clearance. The expression in the brackets, which is the ratio of the theoretical intake volume to the displacement volume, is known as the "volumetric efficiency." To distinguish it from other volumetric efficiencies to be used later, it will be called the "theoretical" or "apparent" volumetric efficiency.

The effect of clearance on the volumetric efficiency is greater for isothermal than for adiabatic compression; but since the former type of compression cycle is not of great industrial importance, quantitative treatment of it will be omitted.

Illustration 5.—What pressure ratio in compressing air adiabatically would give 50 per cent apparent volumetric efficiency if the clearance is 5 per cent?

By Eq. (VII.39), $e_v = \dfrac{V_I}{V_D} = 0.50 = 1 + 0.05 - 0.05r^{\frac{1}{1.40}}$

Solving for r (pressure ratio), $r = 29$

If r were 71, $e_v = 0$ and no flow of gas through the compressor would result. In other words, it would be impossible to compress continuously any diatomic gas from 1 atm. to a pressure higher than about 1,000 lb. per sq. in. in a single cylinder of clearance greater than 5 per cent.

Illustration 6.—A single-stage double-acting compressor with a 10- by 12-in. cylinder[1] and 6 per cent clearance, running at 175 r.p.m., is to be used to compress methane from 1 lb. per sq. in. gauge and 60°F. to 110 lb. per sq. in. gauge pressure. Calculate the maximum capacity of the compressor expressed in cubic feet per minute at the initial conditions and the theoretical adiabatic horsepower.

Neglecting the volume occupied by the piston rod,

$$\text{Displacement volume} = V_D = \frac{0.785 \times 100 \times 12 \times 2 \times 175}{1,728} = 191 \text{ cu. ft./min.}$$

$$V_I = 191 \left[1 + 0.06 - 0.06 \left(\frac{124.7}{15.7} \right)^{\frac{1}{1.31}} \right] = 147 \text{ cu. ft./min.}$$

$$\text{Hp.} = \frac{1.31 \times 15.7 \times 144 \times 147}{0.31 \times 33,000} \left[1 - \left(\frac{124.7}{15.7} \right)^{0.237} \right] = -27.0$$

STAGE COMPRESSION

General Principles.—Illustration 5 showed that the clearance sets a limit to the pressure ratio that can be achieved in any one cylinder. A much lower limit is fixed by other considerations. From Eq. (VII.23) it is clear that a considerable temperature rise accompanies adiabatic compression. For a diatomic gas ($k = 1.40$) taken into the cylinder at 80°F., the temperature at the end of the adiabatic compression stroke would be 595°F. for a pressure ratio of 10. It would be difficult to find a lubricant that would be satisfactory at such a high temperature, not to mention the danger of combustion if the gas contained oxygen. A mechanical difficulty in the way of a high ratio in one cylinder arises from the fact that the cylinder would have to be large to accommodate the large volume of low-pressure gas and yet strong enough to withstand the high pressure. This would result in a clumsy, expensive cylinder if high-pressure ratios were attempted in one cylinder.

For these reasons and for one other very important one, which will be developed later, the pressure ratio attainable in any one cylinder is limited to 10 at the very most and generally to considerably less. Consequently, for pressures above about 100 lb. per sq. in. gauge, it is essential that the compression be carried out in more than one step or stage;

[1] In giving cylinder dimensions, the first figure is always the internal diameter and the second the length of stroke.

and since one of the difficulties is due to the temperature rise in compression, it is essential to cool the gas between stages by means of intercoolers.

To develop quantitative relationships applying to stage compression, consider the idealized two-stage cycle shown on a pV diagram in Fig. VII.5. Line 2-1 represents the suction stroke of the first stage and 1-3 the compression stroke. The gas, compressed in the first cylinder to an intermediate pressure p_i, is discharged to an intercooler, where it is cooled at constant pressure to a temperature approaching the initial temperature of the gas before compression. Line 3-4 represents the discharge stroke in the first cylinder. The cooled gas still at p_i but of smaller volume (V_4 instead of V_3) is then admitted to the second cylinder (suction stroke 8-4), compressed along 4-6 to pressure p_2, and discharged
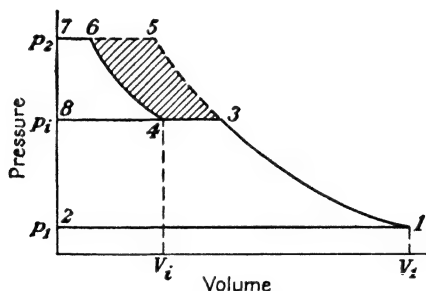
FIG. VII.5.—Ideal two-stage compression cycle.

to a final cooler (discharge stroke 6-7). The work of the first cylinder is represented by the area $\overline{2138}$ and of the second cylinder by $\overline{4678}$; the total work for the mass of gas corresponding to the original intake volume V_1 is the sum of the two areas. If the compression from p_1 to p_2 had been carried out in a single stage as shown by the compression stroke 1-5, the work would have been equal to the area $\overline{2157}$. Consequently, we see that the two-stage work is smaller than the single-stage work by the area $\overline{4356}$. This demonstrates another important advantage of stage compression, viz., a reduction in the work. By dividing the over-all pressure ratio among several stages with cooling between each pair, it is clear that further saving in work could be effected. In Fig. VII.6 let 2-9 represent adiabatic compression from p_1 to p_2 and 2-11 represent isothermal compression. The step line 2-3-4-5-6-7-8-10 represents four-stage adiabatic compression with intercooling always back to the initial temperature of the intake gas along the isotherm 2-11. The shaded area represents the saving in work effected by the use of stages. The limit to the saving in work that can be effected by staging is the area $\overline{2\text{-}11\text{-}9\text{-}2}$ representing the difference between adiabatic and isothermal compression, and this obviously would require an infinite number of

stages. We see, therefore, that the saving in work due to the use of more than one stage is purely a matter of approach to isothermal compression. From this standpoint a large number of stages is indicated, but certain practical considerations limit the number to six at the most, as will be briefly discussed later (page 285).
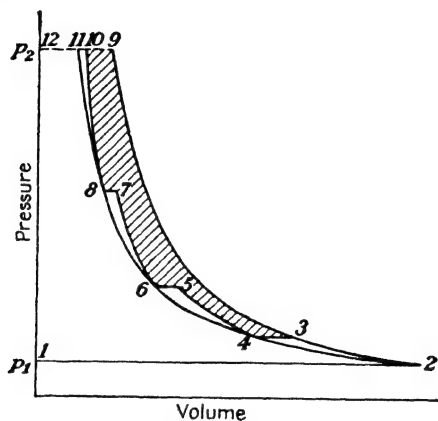
FIG. VII.6.—Diagram illustrating maximum saving in work by stage compression.

Work of Stage Compressors.—In Fig. VII.5, the work for the two-stage cycle is clearly seen to be the sum of the works of two single-stage cycles and may be represented analytically as follows:

$$W \text{ (2 stage)} = \frac{kp_1V_1}{k-1}\left[1 - \left(\frac{p_i}{p_1}\right)^{\frac{k-1}{k}}\right] + \frac{kp_iV_i}{k-1}\left[1 - \left(\frac{p_2}{p_i}\right)^{\frac{k-1}{k}}\right] \quad \text{(VII.40)}$$

This involves the usual assumptions, the most important of which are (1) ideal gas and (2) constant ratio of specific heats and (3) that compression is adiabatic and reversible. If we now assume perfect intercooling, *i.e.*, that the compressed gas is cooled to the temperature of the intake gas, we can write,

$$p_1V_1 = p_iV_i$$

and Eq. (VII.40) is transformed to

$$W \text{ (2 stage)} = \frac{kp_1V_1}{k-1}\left[2 - \left(\frac{p_i}{p_1}\right)^{\frac{k-1}{k}} - \left(\frac{p_2}{p_i}\right)^{\frac{k-1}{k}}\right] \quad \text{(VII.41)}$$

By following the same procedure for more stages we can readily generalize this equation. Thus, for n stages,

$$W = \frac{kp_1V_1}{k-1}\left\{n - \left(\frac{p_{i1}}{p_1}\right)^{\epsilon} - \left(\frac{p_{i2}}{p_{i1}}\right)^{\epsilon} - \left(\frac{p_{i3}}{p_{i2}}\right)^{\epsilon} - \cdots - \left[\frac{p_2}{p_{i(n-1)}}\right]^{\epsilon}\right\} \quad \text{(VII.42)}$$

where $\epsilon = (k-1)/k$.

$p_{i1}, p_{i2}, \cdots, p_{i(n-1)}$ = discharge pressures from stages $1, 2, \cdots,$
$$n - 1.$$

These interstage pressures can have any set of values we choose between the limits p_1 and p_2; but there is presumably one particular set that makes the work a minimum, and this is the set to use. To find the necessary condition for minimum work, let us consider each interstage pressure to vary independently of the others and apply the usual criterion for a minimum, *viz.*,

$$\frac{\partial W}{\partial p_{i1}} = 0, \qquad \frac{\partial W}{\partial p_{i2}} = 0, \text{ etc.} \qquad \text{(VII.43)}$$

Differentiating Eq. (VII.42) and applying Eq. (VII.43),

$$\frac{\partial W}{\partial p_{i1}} = \frac{kp_1V_1}{k-1}\left(-\frac{\epsilon p_{i1}^{\epsilon-1}}{p_1^\epsilon} + \epsilon p_{i2}^\epsilon \, p_{i1}^{-\epsilon-1}\right) = 0$$

and hence
$$p_{i2}^\epsilon p_{i1}^{-\epsilon-1} = p_{i1}^{\epsilon-1} p_1^{-\epsilon}$$

or
$$p_{i1}^2 = p_1 p_{i2} \qquad \text{(VII.44)}$$

Similarly from $\partial W/\partial p_{i2} = 0$, $\partial W/\partial p_{i3} = 0$, etc., we get

$$p_{i2}^2 = p_{i1} p_{i3} \qquad \text{(VII.45)}$$
$$p_{i3}^2 = p_{i2} p_{i4} \qquad \text{(VII.46)}$$
$$p_{i(n-1)}^2 = p_{i(n-2)} p_2 \qquad \text{(VII.47)}$$

From these last four equations, one can write

$$\frac{p_{i1}}{p_1} = \frac{p_{i2}}{p_{i1}} = \frac{p_{i3}}{p_{i2}} = \cdots = \frac{p_2}{p_{i(n-1)}} = r$$

or the pressure ratio r is the same in all stages. The condition for minimum work, therefore, is that the pressure ratio and hence the work shall be the same in all stages.

Since
$$r_1 \times r_2 \times r_3 \times \cdots \times r_n = \frac{p_2}{p_1}$$

then
$$r^n = \frac{p_2}{p_1}$$

and
$$r = \sqrt[n]{\frac{p_2}{p_1}} \qquad \text{(VII.48)}$$

Substituting Eq. (VII.48) in Eq. (VII.42),

$$W \text{ (}n \text{ stages)} = \frac{nkp_1V_1}{k-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{nk}}\right] \qquad \text{(VII.49)}$$

Compressors are generally designed to give approximately equal work in all stages, not only because of the fact that this leads to the minimum work but also because it is desirable from a purely mechanical standpoint.

Effect of Clearance.—As with single-stage compressors, it can be shown that the clearance does not affect the work provided that the actual intake volume is used in place of the displacement volume.

The volumetric (apparent) efficiency of a multistage machine is determined primarily by the clearance in the first stage because whatever gas is taken into the first-stage cylinder must (barring leakage) pass through the others. Thus, we can write from Eq. (VII.39),

$$e_{v1} \text{ (volumetric efficiency of first stage)} = 1 + c_1 - c_1 \left(\frac{p_i}{p_1}\right)^{\frac{1}{k}}$$

where p_i is the first-stage discharge pressure.

If all displacements and clearances are properly proportioned in accordance with the principle of least work, then the over-all volumetric efficiency, which is the same as that of the first stage, is given by

$$e_v = 1 + c_1 - c_1 \left(\frac{p_2}{p_1}\right)^{\frac{1}{nk}} \tag{VII.50}$$

where c_1 is still the clearance in the first stage and p_2/p_1 is the over-all pressure ratio for the multistage compressor. In order to have this true, there must be a definite relationship between the displacements, clearances, and pressures for any two stages. Thus, for the first two stages we must have

$$\frac{V_{D1}}{V_{D2}} = \left(\frac{p_2}{p_1}\right)^{\frac{1}{2}} \left[\frac{1 + c_2 - c_2 \left(\frac{p_2}{p_1}\right)^{\frac{1}{2k}}}{1 + c_1 - c_1 \left(\frac{p_2}{p_1}\right)^{\frac{1}{2k}}}\right] \tag{VII.51}$$

where 1 and 2 refer to the first and second stages, respectively, and p_2 is the discharge pressure from the second stage. This equation follows at once from the fact that the ratio of the intake volumes of any two stages equals the inverse pressure ratio.

Illustration 7.—Compare the theoretical adiabatic horsepower to compress 1,000 cu. ft. of helium per minute from standard atmospheric pressure and 80°F. to 200 lb. per sq. in. gauge (1) in a single stage and (2) in two stages.

For a monatomic gas $k = 1.67$

$$\text{Hp. (single stage)} = \frac{1.67 \times 14.7 \times 144 \times 1,000}{0.67 \times 33,000}\left[1 - \left(\frac{215}{14.7}\right)^{0.401}\right] = -308$$

$$\text{Hp. (2 stage)} = \frac{2 \times 1.67 \times 14.7 \times 144 \times 1,000}{0.67 \times 33,000}\left[1 - \left(\frac{215}{14.7}\right)^{0.200}\right] = -228$$

The minus sign merely indicates that work done on a system is negative according to the convention established.

Illustration 8.—Hydrogen is to be compressed in four stages from 14.7 lb. per sq. in. abs. to 3,000 lb. per sq. in. gauge.   What should the pressures between stages be?

Make the usual simplifying assumptions, such as ideal gas, adiabatic and reversible, perfect intercooling, etc.

By Eq. (VII.48), r per stage $= \sqrt[4]{\dfrac{3{,}015}{14.7}} = 3.78$

Intermediate pressures are

First intercooler, $3.78 \times 14.7 = 55.5$ lb./sq. in. $= 3.78$ atm.
Second intercooler, $3.78 \times 55.5 = 210.0$ lb./sq. in. $= 14.3$ atm.
Third intercooler, $3.78 \times 210 = 795$ lb./sq. in. $= 54.1$ atm.

Illustration 9.—A two-stage compressor is to take hydrogen at the rate of 300 cu. ft. per min. at 80°F. and standard atmospheric pressure and deliver it at 225 lb. per sq. in. gauge.   If the clearance in the first cylinder is 0.04 and in the second 0.06, what should be the displacement of each cylinder in cubic feet per minute?

On the usual assumptions common to compressor problems, volumetric efficiency of the first stage is given by Eq. (VII.50).

$$e_{v1} = 1 + 0.04 - 0.04 \left(\frac{240}{14.7}\right)^{\frac{1}{2 \times 1.41}} = 0.932$$

$$\therefore V_{D1} = \frac{300}{0.932} = 322 \text{ cu. ft./min.}$$

By Eq. (VII.51),

$$\frac{V_{D1}}{V_{D2}} = \sqrt{\frac{240}{14.7}} \left[\frac{1 + 0.06 - 0.06(16.3)^{\frac{1}{2.82}}}{1 + 0.04 - 0.04(16.3)^{\frac{1}{2.82}}}\right] = 3.90$$

$$\therefore V_{D2} = \frac{322}{3.90} = 82.5 \text{ cu. ft./min.}$$

Nonideal Gas.—The work of multistage compressors can also be obtained from a thermodynamic diagram in case it is not permissible to assume ideal gases.   A three-stage compression is represented on the TS diagram, as shown in Fig. VII.7.   Path 1-2 at constant entropy represents a reversible adiabatic compression from $p_1 T_1$ to $p_2 T_2$. Path 2-3 is the constant-pressure intercooling back to T_1, 3-4 the compression stroke in the second stage, etc.   The work per pound or per mole in each stage is obtained from the difference of the enthalpies at the two ends of the constant-entropy lines.   The principle of equal work in all stages could be applied by finding (graphically by trial) the proper values of the intermediate pressures p_2 and p_4 to satisfy the condition that ΔH should be the same for all the constant-entropy lines.   This would presumably give the minimum total work and locate the best intermediate pressures, though no definite proof of the fact has been attempted.

Work Chart.—Figure VII.8 is a chart that makes it possible to obtain in very simple fashion the work for the compression of any gas for any value of k between the two limiting ones of 1.67 and 1.00. This chart is constructed from the equations already derived for the case of reversible adiabatic compression of an ideal gas. The chart is direct reading only for single-stage compressors and for one intake temperature; but, for more than one stage and for other temperatures, simple rules are
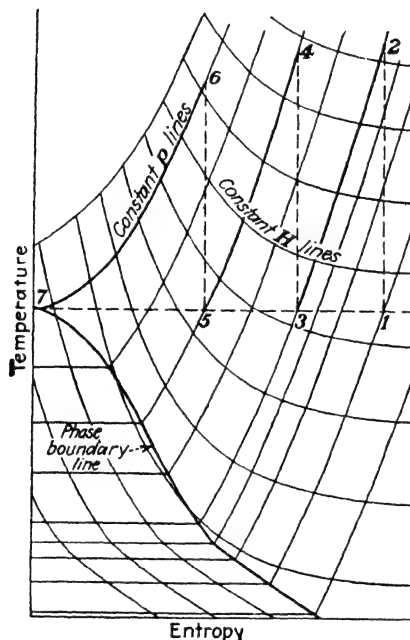
Fɪɢ. VII.7.—Three-stage compression of carbon dioxide on a temperature-entropy diagram.

given for converting the value read from the chart to the desired quantity. The following illustrates the use of this chart.

Illustration 10.—Solve part (2) of Illustration 7 with the chart.

$$r \text{ per stage } = \sqrt{\frac{215}{14.7}} = 3.82$$

From the chart, $W = 0.730$ hp.-hr. per lb.-mole. Correcting to two-stage work and 80°F.,

$$W = 0.730 \times \tfrac{5\,4\,0}{5\,0\,0} \times 2 = 1.49$$
$$\text{Lb.-moles/min.} = \frac{1,000 \times 14.7}{10.72 \times 540} = 2.54$$
$$\text{Total work } = 2.54 \times 1.49 = 3.79 \text{ hp.-hr./min.}$$
$$\text{Hp. } = 3.79 \times 60 = 227$$

Because of the various calculations to be made in this particular case, little is gained by the use of the chart, but it will save calculation in some cases. It is possible to devise a direct-reading chart to cover all the variables here considered, but its complexity tends to defeat its purpose.

Number of Stages.—The desirable number of stages to use in any given case is determined by striking a rough balance between the advantages such as lower cost of power, better volumetric efficiency, etc., and the increased cost of the equipment. No hard-and-fast rule can be
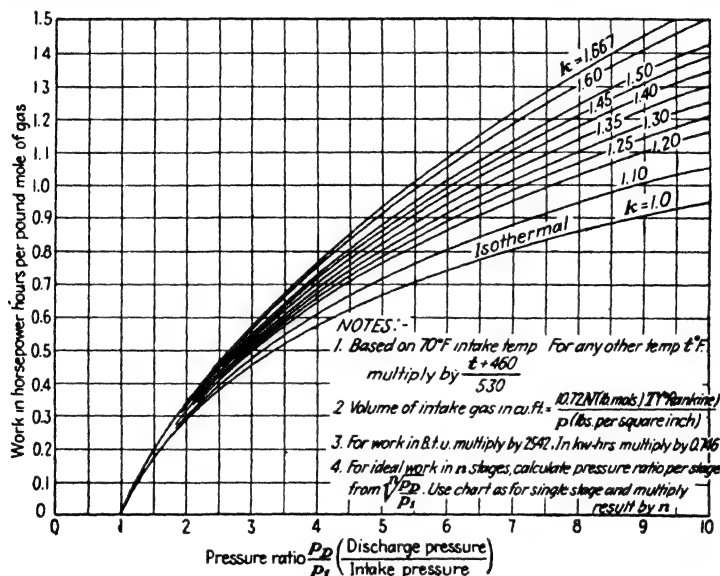
FIG. VII.8.—Calculated work of compression for ideal gas in an ideal single-stage compressor.

given, but in general the maximum pressure ratio in any one stage of large multistage compressors would lie between 3 and 5, with a somewhat higher ratio for single-stage machines. The following tabulation is a very rough guide to the maximum gauge pressures commonly used. Pressure is in pounds per square inch.

Single stage	2 stage	3 stage	4 stage
80	400	1,200	3,000

The 300-atm. compressors used in some of the modern high-pressure processes are commonly six-stage duplex machines, though some four- and five-stage machines are also in use. The highest pressure for which

commercial compressors have been built is 15,000 lb. per sq. in., which is used in some of the modern high-pressure synthesis processes. These have generally been six- or seven-stage machines, though as many as nine stages have been used.

Small compressors for experimental purposes are generally used with much higher pressure ratios because the saving due to lower power and increased volumetric efficiency is not a very important item. Thus small compressors for 1,000 to 1,200 lb. pressure have only two stages, and three-stage machines compress to as high as 4,500 lb. per sq. in. The well-known Hofer compressor goes to 1,000 atm. in five stages. A four-stage machine has been built to operate against a maximum pressure of 4,000 atm.

From what has been said about the effect of clearance, it will be evident that a single-stage reciprocating compressor cannot be expected to produce a very high vacuum. Two-stage reciprocating vacuum pumps are built, and they will produce vacuums of the order of 5 to 10 mm. Hg. Because of the very large displacement required, it does not pay to use more than two stages; for higher vacuums, rotary pumps or steam-jet pumps are employed.

COMPRESSOR AND EXPANDER EFFICIENCIES

Up to this point we have been considering idealized compressors in order to simplify the analysis. We now propose to discuss briefly some of the most important ways in which actual compressors deviate from the ideal behavior we have assumed, pointing out the effect on the work requirement and on the volumetric efficiency.

Some of the most important of the irreversible effects that take place in the compression of a gas in a reciprocating compressor may be summarized as follows:

1. Mechanical friction between moving and stationary parts in contact, such as piston and cylinder, piston rod and stuffing box, crosshead and its bedplate, etc.

2. Throttling (fluid friction) of gas through valves and ports.

3. Leakage of gas past the piston rings and closed valves.

4. Heat interchange between gas and cylinder walls.

Items 1 and 2 clearly result in an increase in the work over that calculated from the ideal cycle. Item 3 also affects the work per pound of fluid, but more directly it brings about a lowering of the volumetric efficiency. We are here referring to a true volumetric efficiency, as distinguished from the apparent one previously used, which may be defined as the ratio of the volume of gas actually taken into the low-pressure cylinder, referred to the pressure and temperature of the gas in the supply main, to the displacement. It may also be defined on the

basis of volume of gas delivered referred to definite intake conditions. The true volumetric efficiency is determined by actual measurement and differs somewhat from the apparent or calculated one previously considered, owing to leakage, to temperature and pressure differences between the gas in the supply main and the gas in the cylinder, and to other departures from the ideal cycle. Thus heat retained by the valves and cylinder walls after the compression stroke is transferred to the gas taken in during the suction stroke, resulting in a lowering of the true volumetric efficiency.

Item 4 tends to reduce the work of compression per pound of gas handled by lowering the exponent of the compression line (*pv* line in compression stroke) to a value below that of the specific-heat ratio. This is a gain, but not a great one, for the cooling of the gas in the cylinder by the water jacket is not very effective and the actual compression approaches much closer to adiabatic than to isothermal conditions.

A work, or power, efficiency may be defined by the equation

$$e_w = \frac{\text{theoretical work (power)}}{\text{actual work (power) input}}$$

There is some confusion in the use of this term because each of the quantities in this ratio can be interpreted in various ways. The actual work is generally taken to mean the input to the compressor shaft in the case of a power-driven machine (also called "brake horsepower") or the indicated work of the steam engine in the case of a compressor driven by a reciprocating steam engine. In some cases, however, the actual work of a power-driven machine is taken to mean the energy supplied to the motor, and hence the efficiency includes that of the motor and the drive. The theoretical work may be taken as the work for reversible isothermal compression between the limits of the supply and the delivered gas pressures, or it may be taken as the isentropic or adiabatic reversible work, which, in the case of a multistage compressor, includes the assumption of perfect intercooling. The theoretical work will also depend on whether one assumes ideal gases or uses the actual properties of the gas in question and on other assumptions involved in the equation used to calculate the theoretical work.

The term "mechanical efficiency" is sometimes used to denote the ratio $\dfrac{\text{indicated work}}{\text{actual work input}}$. The indicated work can be determined from an indicator card if available, or it may be approximated by the calculated adiabatic work based on an equation such as Eq. (VII.49).

In Fig. VII.9 there is represented a type of actual indicator diagram as compared with the idealized diagrams we have been considering. The indicated horsepower may be obtained from the relation

$$\text{Ihp.} = \frac{pLAN}{33,000}$$

where p = mean effective pressure, lb. per sq. in.

L = length of stroke, ft.

A = cross-sectional area of cylinder, sq. in. For double-acting cylinder, multiply by 2 and subtract area due to piston rod.

N = r.p.m.

The mean effective pressure is the area of the card divided by its length times a scale factor to convert to pounds per square inch.

From this brief discussion of compressor efficiencies, it is evident that any numerical values need to be accompanied by some statement
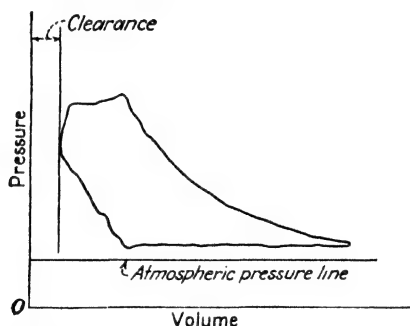
FIG. VII.9.—Typical compressor indicator card.

defining the particular efficiency which is meant if they are to be interpreted accurately.

For the purpose of estimating the work, or power, required to carry out a compression step as a unit operation in a chemical process, which is the usual concern of the chemical engineer, it is convenient to refer to an over-all efficiency. For a motor-driven compressor, we shall take this to mean the ratio between the calculated work for isentropic compression [based on Eq. (VII.49) unless the ideal-gas law is seriously in error] and the electrical-energy input to the prime mover. This figure will vary over rather wide limits, but 75 per cent is probably a fair average for compressors of good size. The same figure will do for a steam-driven machine when the indicated power of the steam engine is substituted for the electrical power. Knowing the average steam rate, *i.e.*, the pounds of steam per indicated horsepower-hour for the type of steam-engine cycle used and condition of the steam, one can then estimate the steam requirement for the process.

For a large centrifugal compressor the ratio of the theoretical adiabatic work to the work delivered to the shaft will also average about 75 per cent.

In the case of any expanding engine, whether reciprocating or of the turbine type or using steam or any gas, the efficiency is defined by

$$e_x = \frac{W}{W_s} \qquad (VII.52)$$

where W = work delivered by the engine per pound of fluid.

W_s = work that would be delivered by an adiabatic and reversible engine operating between the given initial state and the given final pressure.

For an adiabatic engine with negligible velocities in intake and discharge lines, this can be written

$$e_x = \frac{\Delta H}{\Delta H_s} \qquad (VII.53)$$

If the engine is not adiabatic, the work delivered will be greater than or less than ΔH, depending on whether the engine receives heat from the surroundings or loses heat.   In the case of an engine to be used primarily for refrigeration, it is probably best to define the efficiency by Eq. (VII.53) whether it is actually adiabatic or not.

STEAM-JET COMPRESSORS

Steam ejectors have become of considerable importance in recent years for the pumping of large volumes of vapor and gas at low pressures.
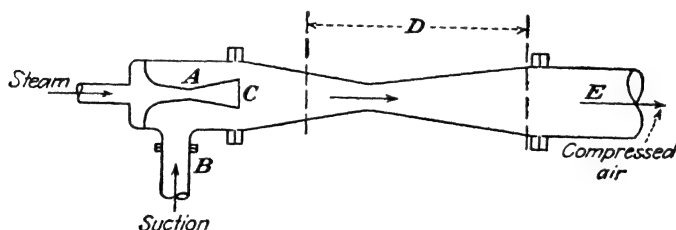
FIG. VII.10.—Diagram of a steam-jet compressor.

Such applications occur, for example, in vacuum distillation, vacuum crystallization, refrigeration, and air conditioning. The principle of the jet, or ejector, pump is illustrated by Fig. VII.10.   Steam is caused to expand in nozzle A, from which it issues with a very high velocity into the mixing space C, where it transfers some of its momentum to the gas or vapor that enters through B owing to the low pressure created by the action of the high-velocity stream.   In the section D, known as the "diffuser," the mixed vapor is compressed, the work of compression resulting from the conversion of kinetic energy, and is discharged through E into a condenser or into the second stage of a similar pump.   The net result is a compression of gas from a low pressure at B to a higher pressure at E at the expense of energy in the steam.

The action of the ejector can be made clearer by considering it from a quantitative standpoint. The treatment given here follows essentially that published by Kalustian.[1]

Let H_1 = enthalpy of the initial or motive steam at pressure p_1.

H_2 = enthalpy of the steam after reversible adiabatic expansion to p_2, the pressure of gas entering the pump from the space to be evacuated.

e_1 = efficiency of the nozzle.

By definition,

$$e_1 = \frac{H_1 - H_2'}{H_1 - H_2} \qquad \text{(VII.54)}$$

where H_2' = enthalpy of the steam after the actual expansion in the nozzle.

$H_1 - H_2$ = theoretical work obtainable from the steam by expansion.

$H_1 - H_2'$ = actual work.

Let H_3 = enthalpy of the mixture (motive power fluid plus fluid being compressed) at the start of the compression in the diffuser section.

H_4 = enthalpy of the compressed mixture at the end of the diffuser, assuming isentropic compression.

$$\text{Ideal work of compression} = H_4 - H_3$$

Let e_2 = efficiency of compression.

Then $$\text{Actual work} = \frac{H_4 - H_3}{e_2}$$

All the above quantities are per pound of fluid.

Let m_1 = pounds of motive steam.

m_2 = pounds of entrained gas or vapor (assumed to be water vapor in the following analysis).

The actual work obtainable from the expansion of the motive steam is less than the theoretical not only because of friction in the nozzle, which is taken account of by the factor e_1, but there is a further loss in available energy in the transfer of momentum from the high-speed jet to the relatively slow-moving entrained vapor. Calling the efficiency of this transfer e_3, the total net available work from the jet = $m_1 e_1 e_3 (H_1 - H_2)$.

Equating this to $(m_1 + m_2)[(H_4 - H_3)/e_2]$, the actual work required for the compression, we have

$$\frac{m_1}{m_2} \text{ (actual)} = \frac{H_4 - H_3}{(H_1 - H_2)e_1 e_2 e_3 - (H_4 - H_3)} \qquad \text{(VII.55)}$$

[1] KALUSTIAN, P., *Refrigerating Eng.*, **28**, 188–193 (1934).

This equation must be solved by trial because H_3 and H_4 are not known until the quality at state 3 is known and this, in turn, depends on m_1 and m_2. Assuming no superheat and no enthalpy change due to mixing, a balance on the mixing process gives

$$x_3(m_1 + m_2) = x_2'' m_1 + x_4 m_2$$

or
$$x_3 = \frac{x_2'' m_1 + x_4 m_2}{m_1 + m_2} \qquad (VII.56)$$

x_2'' is the quality of motive steam after expansion to p_2, the pressure in the suction line, and after loss of kinetic energy in the entraining process, and x_4 is the quality of the entrained steam. x_2'' is related to x_2', the quality after expansion but before the entrainment step, by the equation

$$(1 - e_3)(H_1 - H_2') = (x_2'' - x_2')L \qquad (VII.57)$$

where L is the latent heat of vaporization at the low pressure of the expanded steam. x_2', in turn, is related to x_2, quality after *isentropic* expansion, in a similar way,

$$(1 - e_1)(H_1 - H_2) = (x_2' - x_2)L \qquad (VII.58)$$

Equations (VII.57) and (VII.58) are derived from energy balances on the respective processes. Thus $(1 - e_3)(H_1 - H_2')$ is the kinetic energy dissipated and therefore converted to internal energy in the transfer of momentum. This energy is utilized in drying the vapor and hence equals $(x_2'' - x_2')L$.

From the extensive tests on turbine nozzles, values of the nozzle efficiency are well known. They may vary from 0.85, to 0.95, depending on conditions. e_2 may be assumed to be about 0.80; e_3 may be calculated from the principle of the conservation of momentum, and values so obtained are found to be in good agreement with actual tests on the steam consumption of ejectors.

The minimum possible amount of steam required would be given by Eq. (VII.55) when e_1, e_2, and $e_3 = 1.0$. For this special case, however, the equation can be simplified so as to avoid a trial solution by noting that the work obtainable from the motive steam if expanded from the pressure which obtains at the end of the diffuser section to the pressure of the entrained vapor is exactly the same as the work which has to be done to compress this steam in the diffuser, since all changes are assumed to be reversible in this ideal case. Consequently, the net result is the same as if the motive steam expanded only to the pressure at the end of the diffuser and as if only the entrained vapor were compressed. In other words, the work to compress the entrained vapor from the pressure p_2 to the pressure at the exit from the pump is obtained from the expan-

sion of the motive steam from p_1 to the pressure at the pump exit.   Then we have

$$\frac{m_1}{m_2} = \frac{H_7 - H_6}{H_1 - H_5}$$ (VII.59)

where H_1 = same as before.

H_5 = enthalpy of the motive steam after isentropic expansion to the pressure of the compressed mixture leaving the diffuser.

H_6 = enthalpy of entrained gas or vapor.

H_7 = enthalpy of entrained gas or vapor after isentropic compression from the pressure at which it enters the jet pump to the pressure after the diffuser.

A jet pump can, of course, use fluids other than steam as the motive power.   Very little has been done to investigate this possibility, which should be of particular interest to chemical engineers.   It is suggested that calculations and experimental data in this field might prove interesting.[1]

Illustration 11.—Water is to be evaporated at 40°F., compressed by a steam jet using saturated steam at 100 lb. per sq. in. abs. and condensed at an absolute pressure of 1 lb. per sq. in.   (1) What is the minimum possible amount of motive steam per pound of water evaporated?   (2) What is the theoretical velocity of the steam from the nozzle?   The actual velocity?   (3) Estimate the actual steam consumption.

1. An absolute pressure of 1 lb. per sq. in. corresponds to a temperature of 101.7°F., which is readily obtainable with ordinary cooling water.

All properties of steam will be taken from the Keenan-Keyes tables or Mollier chart.

H_1 (enthalpy of initial motive steam of quality 1.00) = 1,187 B.t.u./lb.

H_5 (enthalpy of motive steam after isentropic expansion to 1 lb./sq. in.) = 896

H_6 (enthalpy of entrained vapor, assumed to be saturated steam at 40°F.) = 1,079

H_7 (enthalpy of entrained vapor after isentropic compression to 1 lb./sq. in. abs.) = 1,231.3

From Eq. (VII.59),

$$\frac{m_1}{m_2} = 0.523 \text{ lb. of motive steam per lb. of entrained steam}$$

2. The theoretical velocity of the steam jet issuing from the nozzle would be given by Eq. (VIII.43), which can be written

$$u_2 = 223.8 \sqrt{H_1 - H_2}$$

when u_2 is in feet per second and H in B.t.u. per pound.   For the actual velocity we can write

$$u_2 \text{ (actual)} = 223.8 \sqrt{e_1 \, \Delta H}$$

[1] Since this was written a paper has appeared [L. T. Work and V. W. Haedrich, *Ind. Eng. Chem.*, **31**, 464–477 (1939)] giving some data on ejectors using several organic vapors as primary or motive fluid.   This paper also refers to several earlier papers dealing with this subject.

$H_1 = 1,187$ and $H_2 = 798$ (isentropic expansion to 0.1217 lb./sq. in.,

the vapor pressure of water at 40°F.)

$$u_2 \text{ (theoretical)} = 223.8 \sqrt{1,187 - 798} \text{ ft./sec.}$$
$$= 4,400 \text{ ft./sec.}$$

If the nozzle efficiency were 85 per cent, the actual velocity would be 4,050 ft. per sec.

3. To estimate the actual steam consumption the following efficiencies will be used:

$$e_1 = 0.85$$
$$e_2 = 0.80$$
$$e_3 = 0.65$$

x_2 (quality after isentropic expansion of motive steam to 0.1217 lb./sq. in.) $= 0.739$

$$H_1 = 1,187, \qquad H_2 = 798, \qquad H_2' \text{ [by Eq. (VII.54)]} = 857$$
$$x_2' \text{ [by Eq. (VII.58)]} = 0.793$$
$$x_2'' \text{ [by Eq. (VII.57)]} = 0.901$$

Assume as a trial value that $x_3 = 0.930$; then

$$H_3 = 1,002$$

H_4 (after isentropic compression from state 3) $= 1,125$

From Eq. (VII.55), $\dfrac{m_1}{m_3} = 2.52$

Assuming $x_4 = 1.00$, x_3 from Eq. (VII.56) $= 0.931$

which checks the trial value.

Note that the actual steam requirement is nearly five times the theoretical.

JOULE-THOMSON, OR THROTTLING, EXPANSION

Fundamental Principles.—Up to this point, the discussion of expansion has been confined to the reversible type, which is simply the opposite of compression.   In fact, we have said very little about expansion, but all the formulas developed in this chapter apply as well to reversible expansion as to compression.   We shall have more to say about this type of expansion in later sections dealing with refrigeration and with the production of very low temperatures.   In the remainder of this chapter we shall deal with an irreversible type of expansion, which naturally has no counterpart in compression.

When gas stored in a constant-volume container under elevated pressure is released through a valve to a lower pressure, for example, to the atmosphere, it does no useful work.   The same gas could have been expanded under conditions such that external work of a useful character would have been obtained, and this work could be utilized to recompress the gas.   In the absence of any mechanism whereby the expanding gas can do work, the expansion is said to be a "free expansion," and it is obviously irreversible.

A batchwise expansion such as this is sometimes known as a "Joule expansion."   It is less important industrially than a related expansion

known generally as a "Joule-Thomson expansion," which occurs in a continuous flow system. We shall defer discussion of the Joule expansion until later (page 305) and pass on to the Joule-Thomson expansion (also known as a "throttling process").

This type of expansion, which we have already referred to on several occasions but have not considered in detail, occurs when a fluid, continuously maintained at the constant pressure p_1, suffers a pressure drop through a valve, porous plug, or other obstruction in the line and flows out into a space continuously maintained at the pressure p_2, the process occurring under adiabatic conditions. For the moment, we shall consider a process that is somewhat simpler from a theoretical standpoint, *viz.*, one in which the throttle is followed by a heat exchanger where sufficient heat is added to or removed from the fluid to bring it back to the initial temperature. This process will be referred to as a "constant-temperature throttling expansion." It is obvious that it is not a truly
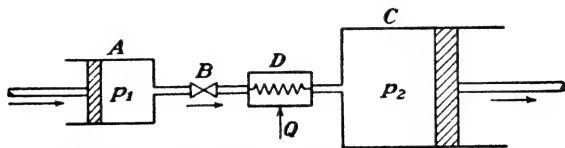
Fig. VII.11.—Constant-temperature throttling expansion.

isothermal process since only the initial and final states are at the same temperature. For purposes of thermodynamic analysis, such a process may be represented by a diagram like that in Fig. VII.11. *A* represents a storage system for gas at pressure p_1 from which gas continuously flows through the throttle *B*. To maintain the pressure in *A* constant, a piston is shown that is assumed to move to the right at just the right speed to compensate for the outflow of gas. (In any actual case the piston, or equivalent volume-displacement device, may be far removed from the actual point of expansion but is bound to be somewhere in the system or the pressure would not remain constant. In any system where fluid is flowing it is customary to imagine a piston pushing the gas into any section isolated for study even though no actual piston is present at that point. This is an aid to the visualization of all the energy terms that must be taken into consideration.) The fluid flows from the throttle *B* through heat exchanger *D* into the storage space *C* in which the pressure is maintained constant at p_2 by proper motion of the piston. Actually, this part of the system may simply be the atmosphere, but again the substitution of an imaginary piston serves to simplify the analysis.

Let us now apply the first law of energy to this process.

$$Q = \Delta E + W \qquad (II.2)$$

The work done by the piston in A per mole of gas flowing from A to $C = -p_1v_1$, where p_1 is the absolute pressure of the fluid in A and v_1 is the molal volume.   Similarly, the work done by the piston in $C = p_2v_2$. If E_1 and E_2 are molal energies of the fluid in states 1 and 2, respectively, then substituting in Eq. (II.2) gives

$$Q = E_2 - E_1 + p_2v_2 - p_1v_1 \tag{VII.60}$$
$$Q = H_2 - H_1 \tag{VII.61}$$

The heat effect accompanying the change between given pressure limits is readily calculated from Eq. (VII.61), given either an equation of state or a thermodynamic diagram.   Thus, from Eq. (III.96), we have at constant temperature

$$\Delta H = - \int_{p_1}^{p_2} T \left(\frac{\partial v}{\partial T}\right)_p dp + \int_{p_1}^{p_2} v \, dp \tag{VII.62}$$

which can also be put in the form

$$\Delta H = \int_{v_1}^{v_2} T \left(\frac{\partial p}{\partial T}\right)_v dv - \int_{v_1}^{v_2} p \, dv + p_2v_2 - p_1v_1 \tag{VII.63}$$

For an ideal gas, it follows at once from Eqs. (VII.61) and (VII.62) that $Q = 0$.   For a van der Waals' gas it is easily seen that

$$Q = a \left(\frac{1}{v_1} - \frac{1}{v_2}\right) + p_2v_2 - p_1v_1 \tag{VII.64}$$

and similarly for other equations of state.

Qualitative Deductions.—Reference to the fundamental equation (VII.60) allows one to make some interesting qualitative deductions about heat effects and temperature changes in such an expansion, in a very simple manner, easy to visualize.   Since, for an ideal gas, E is a function of temperature only and since pv is a constant at constant temperature, it is at once obvious that there will be no heat effect for an isothermal expansion with an ideal gas.   For an actual gas it is clear that E_2 is always greater than E_1 for an isothermal change.   There are always forces of attraction between the molecules of all gases in any state; and as the molecules move apart (expansion) against these forces, energy must be stored in the gas, and it must come from a heat flow into the gas from the surroundings.   Therefore, if one were concerned only with a change in E, there would always be a heat flow in or, if the system were thermally insulated, a drop in temperature.

Considering now the isothermal pv changes, we have three possible cases, *viz.*,

(I) $p_1v_1 = p_2v_2$
(II) $p_1v_1 < p_2v_2$
(III) $p_1v_1 > p_2v_2$

Case (I), which occurs for all real gases in some state, would obviously still lead to a cooling effect. Case (II), which is the situation for all gases at temperatures below their Boyle point and at not too high a pressure, leads to a positive $\Delta(pv)$ and therefore by Eq. (VII.60) to a still greater positive Q or to a cooling effect. Now, when we come to case (III), we find that $\Delta(pv)$ is of opposite sign to ΔE and there will be three subcases depending on the relative numerical magnitudes of the two quantities. These three different subcases lead to three different results as follows:

Case (a), $p_1v_1 - p_2v_2 = E_2 - E_1$
$$\therefore Q = 0$$

and there is no heating or cooling effect. For this particular combination of states, the gas behaves in this type of expansion as if it were ideal.

Case (b), $p_1v_1 - p_2v_2 < E_2 - E_1$

Then Q is positive, and there is still a cooling effect for the adiabatic system.

Case (c), $p_1v_1 - p_2v_2 > E_2 - E_1$

For such a case, by Eq. (VII.60), Q is negative and there will be a heating effect, *i.e.*, heat must be removed to maintain the isothermal conditions postulated. This occurs with such gases as hydrogen and helium at room temperature and not too high a pressure.

Kinetic-energy Correction.—In all this discussion of the irreversible expansion we have tacitly assumed that the only energy possessed by the fluid is that due to its state and defined by its pressure, volume, and temperature. This is strictly true only for a static system. Actually, a flowing gas possesses kinetic energy due to its mass motion. As long as the velocity is small, the kinetic energy is so small that differences in kinetic energy between gas at state (1) and at state (2) (Fig. VII.11) are generally negligible in comparison with the value of ΔH.

Illustration 12.—Air at 80°F. and 100 atm. pressure flowing at an average linear velocity of 1 ft. per sec. expands through an orifice to a pressure of 1 atm. and flows away from the orifice at an average velocity of 20 ft. per sec. Heat flows in to maintain the temperature at 80°F. What error is made in the estimation of the cooling effect by neglecting the kinetic energy?

From a TS chart for air,

$$\Delta H = 256 \text{ B.t.u./lb.-mole for the expansion at constant temperature.}$$

$$\text{Kinetic-energy difference} = \frac{1}{2} m (u_2^2 - u_1^2) = \frac{29}{2 \times 32.2} (400 - 1)$$

$$= 180 \text{ ft.-lb./lb.-mole} = \tfrac{180}{778} \text{ B.t.u.} = 0.231 \text{ B.t.u.}$$

We see that the neglect of kinetic energy makes an error of only 0.1 per cent in this case. It could easily happen, however, that the fluid as it issued from the orifice might have a much higher velocity. Thus, if it were 100 ft. or more per second, the kinetic-energy effect would be appreciable. In all our discussion of the irreversible expansion, we shall assume that any momentary high jet velocities and their corresponding high kinetic energies have been dissipated so that the kinetic energies in the states we are considering are negligible. In the experimental study of the Joule-Thomson expansion, it is common practice to use a porous plug to create the pressure drop and thus minimize the production of high-velocity jets.

Joule-Thomson Effect.—If the expansion illustrated in Fig. VII.11 is carried out adiabatically, Eq. (VII.61) becomes

$$\Delta H = 0 \qquad (VII.65)$$

or, for an infinitesimal change,

$$dH = 0 \qquad (VII.66)$$

This is generally referred to as the "fundamental equation of the Joule-Thomson effect."

From Eqs. (VII.66) and (III.96) we get

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H = \frac{T(\partial v/\partial T)_p - v}{C_p} \qquad (III.97)$$

The Joule-Thomson coefficient μ is clearly a function of the state of the fluid. Integration of Eq. (III.97) would lead to an expression for a finite change in temperature resulting from expansion over a finite pressure range. This ΔT will be referred to as the "integral Joule-Thomson effect" or simply the "Joule-Thomson effect." For ideal gases, evaluation of the right-hand side of Eq. (III.97) by the equation $pv = RT$ leads to the result $\mu = 0$.[1] Furthermore, since μ must be zero for all states of an ideal gas, the latter will show no Joule-Thomson effect. For an

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[1] There is an apparent contradiction here that is worth a brief discussion. The right-hand side of Eq. (III.97) reduces to

$$\frac{(RT/p) - v}{C_p}$$

when the ideal-gas equation is used. But the numerator is the function α, which has already been shown not to become zero as p approaches zero. Consequently, as p approaches zero, μ approaches, not zero, but a finite positive or negative quantity. This is borne out by the experimental data and by use of an equation of state [see Illustration 13]. In explanation of this we may say merely that there is no ideal gas. It is an imaginary gas introduced for convenience and one must not expect an actual gas to have the behavior postulated for an ideal gas even as p approaches zero.

actual gas, we can write

$$\mu \lesseqgtr 0$$

The fact that $\mu = 0$ does not necessarily imply that the gas is ideal or even closely approaching it. In Chap. V we showed that $\mu = 0$ merely led to

$$\frac{v}{T} = \text{constant} = \varphi(p)$$

In other words, any gas for which the volume is linear with the temperature along an isobar will have a zero Joule-Thomson coefficient. Likewise, any actual gas may happen to have a zero Joule-Thomson effect for some particular finite pressure change as shown on page 296.
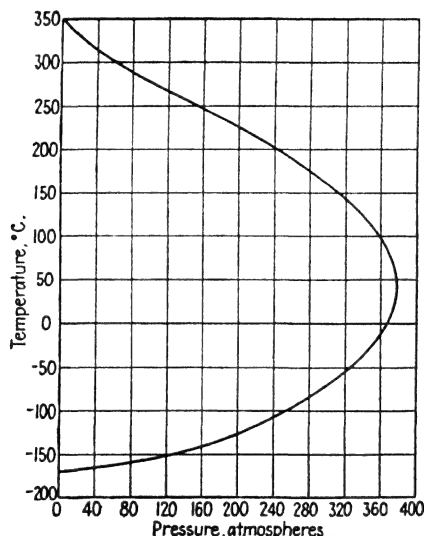
Fig. VII.12.—Joule-Thomson inversion curve for nitrogen. [*Data of Roebuck and Osterberg, Phys. Rev.*, **48**, 450 (1935).]

Inversion Points.—A point at which $\mu = 0$ is known as a "Joule-Thomson inversion point." It is not a unique point, for there will be a whole series of related pressures and temperatures at which $\mu = 0$. In Fig. VII.12, there is shown the inversion curve, or locus of the inversion points, for nitrogen based on the Joule-Thomson measurements of Roebuck and Osterberg.[1] These data and some on argon by the same investigators are the only ones that establish the complete inversion curve. The region inside the curve between $p = 0$ and $p = 375$ atm. consists of states where μ is positive (cooling effect). All the region

[1] ROEBUCK, J. R., and H. OSTERBERG, *Phys. Rev.*, **48**, 450 (1935).

outside represents states where μ is negative.   At any pressure below 375 atm. there are two inversion temperatures, an upper one where μ is going from minus to plus as T is lowered and a lower one where the reverse change occurs.   Beyond 375 atm. there is no inversion at any temperature.   The inversion curve can be calculated from an equation of state though the result can be only approximate unless the equation gives an extremely accurate representation of the behavior of the gas.   In fact such a calculation, if it can be compared with experiment, is a very severe test of an equation of state.

Illustration 13.—Calculate the inversion temperature of the Joule-Thomson coefficient for nitrogen at 100 atm., assuming the Beattie equation of state (V.84).
    By Eq. (III.97) and the equation of state,

$$\mu C_p = \left(-B_0 + \frac{2A_0}{RT} + \frac{4c}{T^3}\right) + \left(\frac{2B_0 b}{RT} - \frac{3A_0 a}{R^2 T^2} + \frac{5B_0 C}{RT^4}\right) p - \left(\frac{6B_0 bc}{R^2 T^4}\right) p^2 = 0$$

For a first approximation we may omit the p^2 term and write

$$p = -\frac{-B_0 + (2A_0/RT) + (4c/T^3)}{(2B_0 b/RT) - (3A_0 a/R^2 T^2) + (5B_0 c/RT^4)}$$

This is a relation between pressure and the inversion temperature.   By substituting various values of T, the following solutions are readily found (values of the constants given in Table V.4):

$$p = 100 \text{ atm.} \qquad T = 589 \text{ and } 44°\text{K.}$$
$$p = 1 \qquad T = 656°\text{K.}$$

The agreement with the experimental curve in Fig. VII.12 is fair for the upper temperature but very poor for the lower temperature. However, disagreement in the latter case is not surprising when one considers that the lower inversion point is actually in the liquid region and the equation of state obviously does not apply to such a condition. At 1 atm. the equation gives only one inversion temperature, whereas two are observed.   In this respect the van der Waals' equation does a better job of predicting the facts than the Beattie equation.
    A semiquantitative idea of the inversion curve for any fluid is obtainable from the law of corresponding states.   Letting $\mu = 0$ in Eq. (III.97) and then writing it in reduced form,

$$T_R \left(\frac{\partial v_R}{\partial T_R}\right)_{p_R} - v_R = 0 \qquad \text{(VII.67)}$$

Differentiating the reduced van der Waals' equation (V.56) and substituting in Eq. (VII.67),

$$T_R = \frac{3(3v_R - 1)^2}{4v_R^2} \qquad \text{(VII.68)}$$

T_R is the reduced inversion temperature of the Joule-Thomson effect.

Eliminating T_R between Eq. (VII.68) and the reduced equation of state,

$$p_R = \frac{9(2v_R - 1)}{v_R^2} \qquad \text{(VII.69)}$$

Combining Eqs. (VII.68) and (VII.69) by elimination of v_R, we would get the equation of the pT inversion curve for any gas in terms of reduced units. As $p_R \to 0$, this equation gives $T_R = \frac{27}{4}$ and $\frac{3}{4}$; also, there is a maximum value of $p_R = 9.0$. The reduced inversion curve is therefore a parabola and is sketched in Fig. VII.13. Comparison with Fig. VII.12 shows that this method predicts quite well the general trend.

On the quantitative side the agreement is only very rough. For nitrogen the maximum pressure at which inversion occurs is 376 atm., or a p_R of 11.2 instead of 9.0 as called for by the theory of corresponding
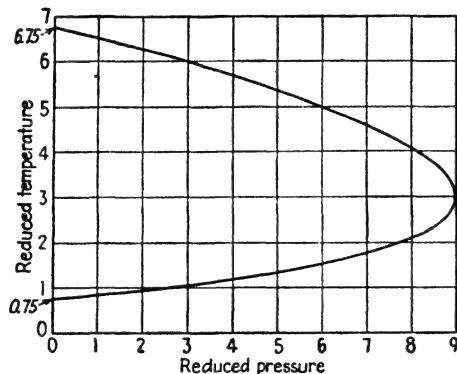
Fig. VII.13.—Reduced inversion curve.

states. Furthermore, the two temperatures for inversion at low pressure are 103.1 and 621°K., or reduced temperatures of 0.82 and 4.93, respectively, compared with the predicted values of 0.75 and 6.75. Similar rough predictions of qualitative value can easily be made for other substances.

Integral Joule-Thomson Effect.—In any actual process, one is always interested in finite changes rather than differential ones, and hence the integral effect is the one of direct interest. The type of problem that arises is as follows: Given a certain fluid in some initial state of elevated pressure, what will be its state after adiabatic throttling expansion to a lower pressure? This is most simply solved with the aid of a thermodynamic diagram, as will be illustrated by the following two examples.

Illustration 14.—Saturated liquid ammonia at 80°F. is expanded through a throttle to a constant lower pressure of 30 lb. per sq. in. abs. What is the state of the ammonia at the lower pressure?

On a Mollier diagram for NH_3, locate the initial point at the intersection of the 80°F. constant-temperature line and the saturated-liquid line. Then proceed at constant H to the intersection with the 30 lb. per sq. in. constant-pressure line, and read the quality. In this particular case, it happens to be more convenient to solve for the quality by Eq. (VI.41) combined with Eq. (VII.65), using the tables of ammonia properties in the "Chemical Engineers' Handbook."[1]

$$H_1 = 132.0$$
$$H_2 = 611.6x + 42.3(1 - x)$$

Since $\qquad\qquad H_1 = H_2 \qquad x = 0.158$

In other words, 15.8 per cent of the liquid has vaporized as a result of the throttling process.

Illustration 16.—Wet steam at 260 lb. per sq. in. absolute pressure is expanded through a throttle to a pressure of 20 lb. per sq. in. abs. The temperature of the expanded steam is 275°F. What was the initial quality?

This illustrates the principle of the throttling calorimeter for determining the quality of wet vapors. It depends on the fact that the adiabatic throttling expansion of wet vapors leads, under many conditions at least, to superheated vapor, and the state of this vapor is uniquely determined by its pressure and temperature.

From the given final pressure and temperature, locate the point on the Mollier (or TS) diagram corresponding to this state, and then proceed at constant H to the intersection with the 260 lb. per sq. in. constant-pressure line. The initial quality is directly read from the diagram[2] as 0.973.

This problem can also readily be solved without the diagram by making use of a table of thermodynamic properties just as was done in the previous illustration.

It is clear that there is a definite limit to the quality that can be measured by this method. The lowest possible quality is that which will just bring the state of the expanded steam to the saturation line; for as long as the expanded fluid remains a mixture, its state will not be definitely determined by its pressure and temperature. Under the conditions of this illustration, it is readily seen that 0.945 is the lowest quality that can be measured by the given expansion. It is of interest to note that at high pressure, for example, 2,000 lb. per sq. in., saturated steam becomes "wet" rather than superheated on throttle expansion.

In the absence of diagrams or tables of properties, various methods can be utilized to calculate the temperature change in a Joule-Thomson or throttling adiabatic expansion. From the fundamental equation of the effect, we have

$$\Delta T = \int_{p_1}^{p_2} \mu \, dp \qquad\qquad (VII.70)$$

Given tabulated values of μ as a function of p and T, one can make a stepwise integration using average values of μ for narrow ranges and finally arrive at a ΔT for the whole expansion.

[1] PERRY, J. H., editor, "Chemical Engineers' Handbook," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

[2] The Mollier chart in "Thermodynamic Properties of Steam" by J. P. Keenan and F. G. Keyes, John Wiley & Sons, Inc., New York, 1936.

In the absence of data on μ, ΔT can be calculated with the aid of an equation of state by the following method, which is closely related to the calculation of the change in enthalpy illustrated in Chap. VI.

From Eq. (III.97), we have

$$\int_{T_1}^{T_1} C_p \, dT = \int_{p_1}^{p_1} T \left(\frac{\partial v}{\partial T} \right)_p dp - \int_{p_1}^{p_1} v \, dp \qquad \text{(VII.71)}$$

or $\int_{T_1}^{T_1} C_p \, dT = -\int_{v_1}^{v_1} T \left(\frac{\partial p}{\partial T} \right)_v dv + \int_{v_1}^{v_1} p \, dv + p_1 v_1 - p_2 v_2 \qquad \text{(VII.72)}^*$

Since a Joule-Thomson expansion generally involves only a small temperature range, we can write

$$\int_{T_1}^{T_1} C_p \, dT = (C_p)_m (T_2 - T_1) \qquad \text{(VII.73)}$$

$T_1 - T_2$ is the integral Joule-Thomson effect, and it is readily calculated from Eqs. (VII.72) and (VII.73), given an equation of state and the mean specific heat of the gas at the lower pressure. The principle underlying this method is more easily visualized with the aid of Fig. VII.14.[1]

Let AB represent the throttling process on a pT diagram. Since $\Delta H = 0$ for such a process, then

$$\Delta H_{AC} = \Delta H_{BC}$$
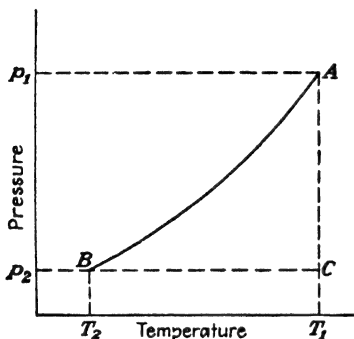
Fig. VII.14.—Integral Joule-Thomson effect.

from the fact that H is a property. ΔH_{AC} is the isothermal change in enthalpy between the given pressure limits at the known initial temperature T_1 and corresponds to the right-hand side of Eq. (VII.71) or (VII.72). ΔH_{BC} is the constant-pressure change in enthalpy at the known low pressure and equals the left-hand side of Eq. (VII.71).

Illustration 16.—Calculate the drop in temperature that would result from the adiabatic throttling expansion of air from 215.2 atm. abs. to 1.2 atm., the air being initially at 0°C.

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* See Eq. (4), Illustration 4, Chap. VI. v_2 is not the final volume corresponding to the end state of the throttling process but the volume at the final pressure and the *initial temperature*. This follows from the fact that the integration of Eq. (III.97) is performed first at constant T and then at constant p.

[1] Note that even if one uses Eq. (VII.72) the integration steps are still represented by Fig. VII.14. We have merely changed the independent variable along the constant T step.

The Beattie-Bridgeman equation of state for air, constants for which appear in Table V.4, will be used. Integration of the right-hand side of Eq. (VII.71) by means of this equation of state has already been performed in Illustration 4 of the preceding chapter. Utilizing the result given there, Eq. (VII.71) becomes

$$T_1 - T_2 = \frac{1}{J(C_p)_m}\left[p_2v_2 - p_1v_1 + \alpha_1\left(\frac{1}{v_1} - \frac{1}{v_2}\right) + \beta_1\left(\frac{1}{v_1^2} - \frac{1}{v_2^2}\right) - \gamma_1\left(\frac{1}{v_1^3} - \frac{1}{v_2^3}\right)\right]$$

(1)

v_1 is obtained from the equation of state by trial. This is quite simple since an almost correct value can be chosen for the first trial from a compressibility-factor chart. v_2 can be calculated with sufficient accuracy from the ideal-gas law.

$$v_1 = 0.1047 \text{ liter/g.-mole}$$
$$v_2 = 18.70 \text{ liter/g.-mole}$$
$$(C_p)_m = 6.95 \text{ g.-cal./g.-mole}$$
$$J = 0.04133 \text{ liter-atm./g.-cal.}$$

Substituting values in Eq. (1),

$$\Delta T = 44.6°C.$$
or $$t_2 = -44.6°C.$$

The experimental value found by Roebuck[1] is 42.8°C.

If the lower pressure is substantially higher than atmospheric the mean C_p can be estimated by one of the methods given in the preceding chapter.

This method should be useful for calculating the Joule-Thomson effect where gas mixtures are involved. If the constants of an equation of state for the individual gases are known, then the constants for the mixture can be obtained by one of the methods given in Chap. V. The Joule-Thomson effect is then calculated just as for a single gas.

The calculation of the Joule-Thomson effect is, as we have just shown, primarily a matter of calculating the change of H for an isothermal expansion. This was discussed in the preceding chapter, and we shall illustrate the use of a few of the methods given there. Thus we may use Fig. VI.14 to solve the problem of illustration 16. From the critical data in Table IV in the Appendix, we find that T_R at 0°C. = 2.06. The two values of p_R are 5.78 and 0.032 atm. From Fig. VI.14,

$$\frac{\Delta H}{T} = 1.15$$
$$\Delta H = 1.15 \times 273 = 314 \text{ c.h.u./lb.-mole}$$

Equating this to $-(C_p)_m(T_2 - T_1)$, we get

$$T_2 - T_1 = -45.2°C.$$

which is a good check on the value obtained from the Beattie-Bridgeman equation.

[1] ROEBUCK, J. R., *Proc. Am. Acad. Arts. Sci.*, **64**, 287–334 (1930).

Equation (VI.35) may also be used to estimate the Joule-Thomson effect directly from an activity-coefficient chart. Thus we have

$$\Delta H^\circ = (C_p)_m \, \Delta T = RT_1 \left(\frac{\partial \ln \gamma}{\partial \ln T_R} \right)_{P_R} \qquad \text{(VI.35)}$$

or

$$\Delta T \text{ (Joule-Thomson effect)} = \frac{RT_1 T_R}{(C_p)_m} \left(\frac{\partial \ln \gamma}{\partial T_R} \right)_{P_R} = \frac{RT_1^2}{(C_p)_m T_c} \left(\frac{\partial \ln \gamma}{\partial T_R} \right)_{P_R}$$
$$\text{(VII.74)}$$

The slope is obtained with sufficient accuracy from the chart by assuming that

$$\frac{\partial \ln \gamma}{\partial T_R} = \frac{\Delta \ln \gamma}{\Delta T_R}$$

and selecting two values of $T_R (T_{R1}$ and $T_{R2})$ near the given initial temperature. Thus, Eq. (VII.74) becomes

$$\Delta T = \frac{RT_1^2 \ln \dfrac{\gamma_1}{\gamma_2}}{(C_p)_m (T_{R1} - T_{R2}) T_c} \qquad \text{(VII.75)}$$

Illustration 17.—Calculate the cooling that occurs when air at 3.2°C. and 185.3 atm. abs. expands adiabatically through a throttle to 1.2 atm.

From the derivation of Eq. (VII.75) it is evident that both the γ's refer to the initial pressure, which is 4.98 in reduced units. The given temperature is a T_R of 2.09, and we shall arbitrarily take $T_{R1} = 2.20$ and $T_{R2} = 2.00$. From the activity-coefficient chart, $\gamma_1 = 0.972$, and $\gamma_2 = 0.922$. Substituting values in Eq. (VII.75),

$$\Delta T = \frac{(1.987)(276.3)^2(2.303) \log \dfrac{0.972}{0.922}}{(6.95)(2.20 - 2.00)(132.4)} = 42.8°C.$$

The experimental value of Roebuck[1] is 39.6°C.

Newton and Dodge[2] applied Eq. (VII.75) to seven cases of Joule-Thomson expansion with good success. They also give a modified equation that can be used when the lower pressure is substantially higher than 1 atm. inasmuch as Eq. (VII.75) is limited to those cases where the gas can be assumed ideal in the low-pressure state.

Comparison of Cooling Effect in Reversible and Irreversible Expansions.—The fall in temperature resulting from a reversible expansion in which useful external work is done, as in an engine cylinder, for example, is readily calculated from Eq. (VII.23), assuming an ideal gas. Thus, if nitrogen at 70°F. and 4 atm. were expanded adiabatically and reversibly to 1 atm., we have

[1] *Loc. cit.*

[2] NEWTON, R. H., and B. F. DODGE, *Ind. Eng. Chem.*, **27**, 577 (1935).

$$T_2 = 530(\tfrac{1}{4})^{\frac{1.40-1}{1.40}}$$
$$= 530 \times 0.674$$
$$= 357°R. \quad \text{or} \quad -103°F.$$

Under these conditions the gas cools 173°F. owing to the expansion. On the other hand, if the same gas (not ideal, of course) were expanded irreversibly in the Joule-Thomson way, application of Eq. (1), Illustration 16, would show a cooling of less than 1°F. In other words, there is a very great difference in the cooling effect resulting from these two expansions for the limiting cases. Any irreversibility in the expansion with work will reduce the temperature drop below that calculated, and one can imagine an expansion in an engine cylinder which is so inefficient that no external work is done and the result is the same as a Joule-Thomson expansion.

JOULE EXPANSION

This type of expansion will be represented diagrammatically as in Fig. VII.15. The process may consist either of the expansion from a
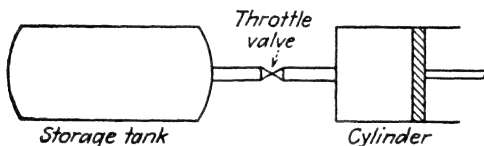
FIG. VII.15.—Joule expansion.

constant pressure in the cylinder to a constant-volume storage tank or of the reverse. A quantitative theory of the former process is obtained in a simple manner by application of the first law if one assumes that the process is adiabatic, or, in other words, neglects any transfer of heat between the fluid and the walls of the storage tank. For this development the following special nomenclature will be used:

N = number of moles (or pounds) of gas.
V_T = total volume of the tank.
Subscripts c and T refer to cylinder and tank, respectively.
Superscripts ['] and [''] refer to initial and final states.
By the first law and assumption of an adiabatic process,

$$Q = \Delta E + W = 0$$

Then
$$\Delta E = N_T'' E_T'' + N_c'' E_c'' - N_T' E_T' - N_c' E_c'$$
$$E_c'' = E_c' = E_c$$
$$W = p_c v_c (N_T' - N_T'')$$
$$N_c'' - N_c' = N_T' - N_T''$$
$$E_c + p_c v_c = H_c$$

Substituting in the first-law expression,

$$\frac{N_T''}{N_T'} = \frac{H_c - E_T'}{H_c - E_T''} \tag{VII.76}$$

If the fluid is an ideal gas and if the initial temperatures and final pressures in both tank and cylinder are assumed equal, the following relations apply:

$$E = \int C_v \, dT + C$$

$$C_v = \frac{R}{k-1}$$

$$E = \frac{RT}{k-1} + C$$

$$H = E + RT = \frac{k}{k-1} RT + C$$

$$N_T' = \frac{p_1 V_T}{RT_1}$$

$$N_T'' = \frac{p_c V_T}{RT_2}$$

where p_1 = initial tank pressure.
T_1 and T_2 = initial and final tank temperatures.
Substituting in Eq. (VII.76),

$$T_2 = T_1 \frac{k p_c}{(k-1)p_1 + p_c} \tag{VII.77}$$

If p_1 is small compared with p_c, Eq. (VII.77) reduces to

$$T_2 = kT_1 \tag{VII.78}$$

Applications of these equations are given in the following illustrations.

Illustration 18.—A storage cylinder for air is completely evacuated and allowed to assume the room temperature of 70°F. The valve is then suddenly opened, and air flows in until the pressure in the cylinder is atmospheric. Assuming air is an ideal gas and neglecting heat transfer from the air to the cylinder walls, estimate the temperature of the air in the cylinder when the pressures have equalized.

In this case, p_1 is so small compared with p_c that Eq. (VII.78) applies and we have

$$T_2 = 1.41 \times 530 = 747°R. \text{ or } 287°F.$$

In a small tank of high heat capacity relative to that of the air, the actual temperature rise would be much less than this because the process would be far from adiabatic, but the larger the tank the more nearly the equation should give the correct result. For an experimental proof of the correctness of the predicted temperature rise see a paper by Oestrich [*Forsch. gebiete Ingenieurw*, **7**, 287–291 (1936)].

Illustration 19.—1. A well-insulated tank of 5,000 cu. ft. capacity is to be used for the storage of steam. Assuming the tank to be filled initially with saturated steam at 1 atm. absolute pressure, how much steam could be stored if the tank were

connected to a source of saturated steam at the constant pressure of 150 lb. per sq. in. abs. and allowed to fill until the pressures are equalized? What will be the condition of the steam in the tank? Neglect heat losses.

Equation (VII.76) is applicable; it will be used on a 1-lb. basis instead of a molal basis.

$$H_c = 1194 \text{ B.t.u./lb.}$$

$$E'_T = 1,150.4 - \frac{14.7 \times 144 \times 26.8}{778} = 1,077.4$$

N''_T and E''_T are obtained by a trial solution. Assume final temperature of steam $(t_2) = 500°F$.

$$v_2 = 3.681 \text{ cu. ft./lb.}$$

$$E''_T = 1,274 - \frac{150 \times 144 \times 3.681}{778} = 1,172$$

$$N'_T = \frac{5,000}{26.8} = 187$$

$$N''_T = \frac{5,000}{3.681} = 1,357$$

Substituting in Eq. (VII.76), $7.27 \neq 5.3$

A few further trials give the solution

$$t_2 = 515°F., \qquad v_2 = 3.747, \qquad N''_T = 1,332$$
$$\text{Steam stored} = 1,145 \text{ lb.}$$

2. Assume that the same tank is filled to 0.75 of its volume with water at 212°F., the remainder of the volume being occupied by saturated steam at 1 atm. abs. Let the tank be connected as before to a source of saturated steam at 150 lb. per sq. in. absolute pressure, and let the steam as it enters the tank be thoroughly mixed with the water so that the steam in the tank is always in equilibrium with the water. How much steam can be expanded into the tank under these conditions when the pressures have equalized? Again neglect heat losses.

If one neglects the mass of steam in the tank compared with that of the water, Eq. (VII.76) applies to this case, with E_T being an energy content of liquid water

$$H_c = 1,194$$
$$E'_T = 180$$
$$E''_T = 330$$
$$N'_T = \frac{5,000 \times 0.75}{0.0167} = 225,000 \text{ lb.}$$
$$\frac{N''_T}{N'_T} = \frac{1,194 - 180}{1,194 - 330} = 1.173$$
$$N''_T = 264,000$$
$$\text{Lb. of steam stored} = 39,000$$

Total volume of water in the tank at the end $= 264,000 \times 0.0181 = 4,780$ cu. ft.

This problem illustrates the principle of a steam accumulator, which is an important device used in many industries where steam demand for a process is quite variable with time. The accumulator takes up the unbalance between the steady supply from the boilers and the fluctuating process demand.

CHAPTER VIII

THERMODYNAMICS OF FLUID FLOW

The quantitative treatment of fluid flow, whether concerned with flow in pipe lines, flow through various measuring devices such as orifices, nozzles, and Venturi tubes, or flow through nozzles for the purpose of power generation, may be based directly on the first and second laws of thermodynamics. It is the purpose of this chapter to show how these two laws and especially the first law may be applied to different fluid-flow problems. One should recognize at the start that the application of thermodynamics can only relate the various energy terms involved and thereby establish the limiting, ideal conditions of flow; it cannot give any information on questions related to mechanism of flow such as the loss of head due to friction. A detailed discussion of frictional effects as well as all detailed descriptions of equipment belong more properly in a text on the unit operations of chemical engineering and will be considered, for the most part, beyond the scope of this book.

A strictly thermodynamic treatment of fluid flow does not require the introduction of any considerations concerning the mechanism of flow. It assumes that all fluids flow in an ideal frictionless manner and there. fore entirely ignores the property of viscosity, which is possessed by all actual fluids, both liquid and gaseous. The theoretical equations derived on this basis will require some modification if they are to describe the behavior of actual fluids. Since it is our aim to carry the thermo-dynamic treatment beyond the point of developing purely theoretical equations so that practical problems can be solved, this will of necessity involve some kinetic considerations. It will be assumed that the reader is already familiar with the elements of fluid-flow mechanism such as the definition of viscosity, the two regions of flow—streamline, or viscous, and turbulent—the chief characteristics of each, and the use of the dimensionless ratio $Du\rho/\mu$ (the Reynolds number Re) in character-izing the conditions of flow.

GENERAL ENERGY EQUATIONS

Figure VIII.1 represents in diagrammatic form any section of a pipe line in which fluid is flowing. We shall assume for all our discussion that the flow is in a steady state. M represents any device such as a pump or a turbine by which the fluid does work on the surroundings or by

which work is done by an outside system on the fluid. Since such work is commonly transmitted to or from the system by a shaft, it will often be referred to as "shaft work" to distinguish it from other forms of work. z is the mean height of the fluid mass at any section of the line above an arbitrarily chosen datum plane.
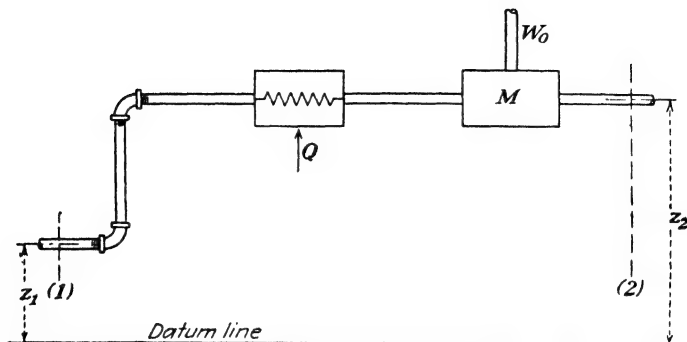
Fig. VIII.1.—Simple fluid-flow line.

Potential- and Kinetic-energy Terms.—We have previously stated the first law of energy by the equation,

$$E_2 - E_1 = Q - W \qquad (VIII.1)$$

where E = total "internal" energy associated with the state of the system.

Q = heat entering the system from the surroundings.

W = work done by the particular system on the surroundings.

The term E includes only those forms of energy which are associated with the forces acting between the ultimate particles, *i.e.*, the atoms, molecules, electrons, etc., and kinetic energy due to their motion. The total amount of such internal energy is uniquely determined when a sufficient number of the usual variables of state have been specified. In the case of a flow system, on the other hand, there are two forms of energy, commonly neglected in many thermodynamic discussions, that must be taken into account in a complete statement of the law of conservation of energy. These two forms are of a quite different character from the forms of energy involved in the E terms because they are associated with large (relatively) masses of fluid rather than with the ultimate particles. These "macroscopic" energy forms are (1) potential energy due to position in a gravitational field and (2) kinetic energy due to mass motion. It is self-evident that, when any mass is conveyed from one level to a higher one, work must be done; conversely, work can be obtained from the reversal of the process. The change in position has

not, as far as one can tell, altered the state of the substance, and therefore
E is unchanged. Nevertheless, the process involved the doing of work;
and since our concept of forces and energy demands that the work
done in increasing the elevation appear as some form of energy and, con-
versely, that the work gained from a lowering of the mass come from some
source of energy, we "invent" a form of energy that is called "potential"
energy. We shall not inquire further into the details of how this form
of energy is stored or released. The quantity of this form of energy
is measured by the product of the weight of the system and the vertical
height above any arbitrarily chosen plane.

It is also evident that a mass in motion possesses kinetic energy
which is entirely separate and distinct from the kinetic energy due to
the motion of the individual particles. The latter form of kinetic
energy is present in a static system and is determined by the variables
of state and hence is included in the E term. The kinetic energy of
mass motion bears no relation to the variables of state and is handled as
a separate energy term, its value being given by the well-known equation

$$\text{Kinetic energy (K.E.)} = \frac{1}{2}\,(\text{mass})(\text{velocity})^2 = \frac{mu^2}{2g} \quad \text{(VIII.2)}$$

where m = total mass of the flowing system.

   u = its velocity relative to a static frame such as the channel in
which the fluid is being conveyed.

   g = acceleration of gravity.[1]

Mean Velocity.—This formulation of the kinetic energy is strictly
correct only for certain ideal conditions. In order to have a clear
understanding of this, it is important to digress for a moment and con-
sider in more detail just what is meant by the velocity term u. It is a
well-known fact that the axial component of the linear velocity of a
fluid in motion in a channel varies throughout the cross section of the
channel. Thus in a circular cross section the velocity is zero at the walls
and increases to a maximum at the center, the curve of velocity vs. dis-
tance from the center varying with the type of flow and the degree of
turbulence. It is common practice to define a mean linear velocity in
feet per second by the equation

$$u = \frac{wv}{A} \quad \text{(VIII.3)}$$

where w = weight rate of flow, lb. per sec.

   v = mean specific volume of the fluid at the point in question,
cu. ft. per lb.

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[1] g is introduced because, in the equations to be developed, the gravitational system
of units will be used. In this system the mass is m/g where m is absolute, or inertial,
mass.

A = cross-sectional area of the flow channel at the given point, sq. ft.

A mean velocity defined by Eq. (VIII.3) does not give the true mean kinetic energy by Eq. (VIII.2). For the special case where the flow is streamline the true mean kinetic energy could be obtained by a summation of the instantaneous values at each point in the cross section. Thus in the case of a circular pipe the velocity-distribution curve is definitely calculable from theory, and it can be shown that the kinetic energy is given by mu^2/g rather than $mu^2/2g$ when u is defined by Eq. (VIII.3). For the case of turbulent flow, which is by far the most common in any practical case, there is the further complication that the fluid possesses not only the kinetic energy of translation in an axial direction but also that due to the crosscurrents and eddies present in turbulent flow. Therefore, Eq. (VIII.2) is true only for an ideal type of flow that is streamline and also shows no variation in velocity across the flow channel. The treatment of actual flow would involve certain correction terms; but fortunately these terms nearly cancel when an energy balance is made between two sections, and the net result is nearly the same as if Eq. (VIII.2) correctly represented the kinetic energy under the actual flow conditions. In the subsequent treatment it will be assumed that the mean kinetic energy of any fluid can be represented with sufficient accuracy by Eq. (VIII.2) using the mean linear velocity defined by Eq. (VIII.3).[1]

In the case of flow accompanied by a transfer of heat, a certain amount of ambiguity is also introduced by the fact that v [Eq. (VIII.3)] varies throughout the cross section and some kind of arbitrary average density must be employed.

Formulation of Energy Equations.—Returning to a consideration of Eq. (VIII.1), we shall have, in addition to the energy forms comprised in E, the potential energy and the kinetic energy just discussed. Q represents the net transfer of heat between the pipe line under consideration and the surroundings. This includes not only any heat added or removed by means of a heat exchanger as shown in Fig. VIII.1 but also any heat loss from the line itself. The work term W may be conveniently divided into two parts, (1) the work done by or on the fluid as it leaves or enters the section under consideration, which is given by the product pv; and (2) the work delivered to or by the machine M, or shaft work. This will

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[1] Some authors prefer to use the more general expression

$$\text{K.E.} = \frac{mu^2}{\alpha g}$$

where α depends on the flow conditions, being 1.0 for viscous flow and approaching 2.0 for turbulent flow.

be represented by W_0 per pound of fluid.   Since there may be more than one machine in the system, W_0 is to be regarded as the algebraic summation of all the shaft-work terms, or the net shaft work.

Let us now apply the first law to the section of pipe line between (1) and (2) in Fig. VIII.1.   The resulting equation is

$$\left(p_2 v_2 + z_2 + \frac{u_2^2}{2g}\right) - \left(p_1 v_1 + z_1 + \frac{u_1^2}{2g}\right) = Q + E_1 - E_2 - W_0 \quad \text{(VIII.4)}$$

in which each term is based on 1 lb. mass of fluid and the same energy units are used throughout.   If E and Q are expressed in thermal units, they should be multiplied by J. W_0 is positive if M is a turbine or other device doing work and negative if M is a pump.   The pressure p is absolute pressure.   Equation (VIII.4) may also be put in the form

$$H_2 - H_1 + z_2 - z_1 + \frac{u_2^2 - u_1^2}{2g} = Q - W_0 \quad \text{(VIII.5)}$$

It may also be put in the following differential form, which is desirable for certain applications:

$$dE + dz + p\,dv + v\,dp + \frac{u\,du}{g} = dQ - dW_0 \quad \text{(VIII.6)}$$

The Bernoulli Theorem.—In many cases there is no machine doing external work, and also the terms of the general energy equation involving Q and the thermodynamic function E are negligible, with the result that Eq. (VIII.4) can be put in the simpler form

$$\left(z_2 + p_2 v_2 + \frac{u_2^2}{2g}\right) - \left(z_1 + p_1 v_1 + \frac{u_1^2}{2g}\right) = 0 \quad \text{(VIII.7)}$$

which involves only mechanical energy terms.   This equation, commonly called Bernoulli's theorem, was well known in hydrodynamics long before the development of the first law of energy.   It assumes frictionless flow since any friction will result in a conversion of other forms of energy into thermal energy and this is accounted for only in the ΔE and Q terms of the general equation.   It is also strictly applicable only to incompressible fluids.

Mechanical-energy Balance.—In the case of a compressible fluid where the pressures at the two sections are quite different, the purely mechanical energy balance represented by Eq. (VIII.7) will lead to incorrect results.   For certain applications many writers have preferred to put the general energy equation (VIII.6) in the following mechanical-energy form,

$$dz + v\,dp + \frac{u\,du}{g} + dF + dW_0 = 0 \quad \text{(VIII.8)}$$

which in integral form becomes

$$z_2 - z_1 + \int_1^2 v \, dp + \frac{u_2^2 - u_1^2}{2g} + \Sigma F + W_0 = 0 \qquad \text{(VIII.9)}$$

The friction term is written as a summation because it is frequently desirable to treat separately friction from various sources. Equation (VIII.8) may be obtained from Eq. (VIII.6) in the following way:

By the first law, $\qquad dQ = dE + dW$

For a *reversible* process, $\qquad dW = p \, dv$

and hence $\qquad\qquad\qquad dQ = dE + p \, dv$

Substitution of this equation in Eq. (VIII.6) gives Eq. (VIII.8) without the dF term. In order to apply the equation to flow in pipe lines and to other cases where friction is not negligible and the flow is not reversible, the dF term is added. It is best regarded as a term necessary to make the equation balance. The necessity for this can readily be seen if we apply Eq. (VIII.8) without the dF term to a Joule-Thomson expansion. It would lead to the following result,

$$v \, dp = 0$$

which is obviously incorrect. Since the dF term is only vaguely defined, Eq. (VIII.8) should be used with caution, for it is easy to be led into an incorrect application. One of the difficulties with the use of Eq. (VIII.8) is that one must have a definite p, v relation in order to integrate it; but a definite point relation between p and v implies a reversible change, and yet the very presence of the F term denotes irreversibility.

Equation in Terms of Fluid Head.—Since every term in Eq. (VIII.4) must be expressed in the same energy units, it is clear that they may all be expressed in terms of potential energy or weight times height, or, since the weight was taken to be unity, in terms of a height or a head, in feet. Thus E may be called the head due to internal energy; z, potential or gravity head; $u^2/2g$, velocity head; pv (static) pressure head, and W_0 the shaft-work head, which, in the case of application to a pumping system, is then called the "total head" developed by the pump. Since the head equivalent to E has little physical meaning, it is probably better to restrict the use of "head" to the mechanical-energy terms. The pressure head is simply that vertical height of a column of the given fluid above a base which will exert the given pressure on this base. In the case of a flow of liquid in a pipe, it is the vertical height above the center line of the pipe to which the liquid will rise in an open-end tube attached to the pipe so that the plane of the tube opening is parallel to the direction of flow. In the case of a gas flow the pressure head is commonly measured by balancing the pressure against a column of some liquid and then converting to the equivalent head of gas. An

equivalent head of any fluid is the vertical height of a column of the fluid that will just balance a given column of the reference fluid. The following very simple relationship holds:

$$h\rho = h_0\rho_0 \qquad (VIII.10)$$

where h_0 and ρ_0 are the head and density, respectively, of a reference fluid and h is the equivalent head in terms of another fluid of density ρ. Thus the equivalent head of hydrogen at 70°F. and 50 lb. per sq. in. absolute pressure for a 6 in. head of water would be

$$h = \frac{6 \times 62.4 \times 359 \times 530 \times 14.7}{12 \times 2.016 \times 492 \times 50} = 1,763 \text{ ft.}$$

Velocity head is directly measured by means of the Pitot tube [to be discussed later (page 336)] in terms of the equivalent head of the fluid used in the manometer. It is of interest to note that in the case of a liquid the velocity head is equal to the height through which the fluid must fall freely under the influence of gravity to attain the given velocity.

The Bernoulli theorem as expressed by Eq. (VIII.7) may now be stated as follows: The total head of a flowing fluid remains constant. Total head in this case is the sum of the gravity head, pressure head, and velocity head. This, of course, neglects all friction in the fluid since Eq. (VIII.7) neglects the Q and ΔE terms, as already pointed out.

From the definitions of static-pressure head h_p and velocity head h_u, it is obvious that the following simple relations can be written,

$$h_p = pv = \frac{p}{\rho} \qquad (VIII.11)$$

or
$$p = h_p\rho \qquad (VIII.12)$$

$$h_u = \frac{u^2}{2g} \qquad (VIII.13)$$

or
$$u = \sqrt{2gh_u} \qquad (VIII.14)$$

Illustration 1.—What is the head of oil of specific gravity 0.85 equivalent to a static pressure of 1 lb. per sq. in.?

By Eq. (VIII.11) $h = \dfrac{1 \times 144}{62.4 \times 0.85} = 2.71 \text{ ft.}$

Illustration 2.—What is the velocity head of CO_2 at 80°F. and 10 lb. per sq. in. gauge pressure flowing at an average linear velocity of 10 ft. per sec.? What is the equivalent velocity head referred to water?

By Eq. (VIII.13), $h_u = \dfrac{100}{32.2 \times 2} = 1.553 \text{ ft. } CO_2$

ρ_{CO_2} (assuming ideal gas) $= \dfrac{44 \times 492 \times 24.7}{359 \times 540 \times 14.7} = 0.1877 \text{ lb./cu. ft.}$

By Eq. (VIII.10),   Equivalent head $= \dfrac{1.553 \times 12 \times 0.1877}{62.4} = 0.0561 \text{ in. } H_2O$

APPLICATIONS TO MEASUREMENT OF LIQUID-FLOW RATE IN HEAD METERS

Types of Head Meters.—This class includes the commonest and most important types of fluid-measuring devices, *viz.*, the orifice, Venturi tube, Pitot tube, and flow nozzle. The general principle is the same in all cases, in that the flow is caused, by a suitable insertion in the line, to produce an observable difference in pressure or head which can be related to the flow rate. The relation between the rate of flow and the differential head is obtained by applying one of the general energy equations and developing it for the special conditions.
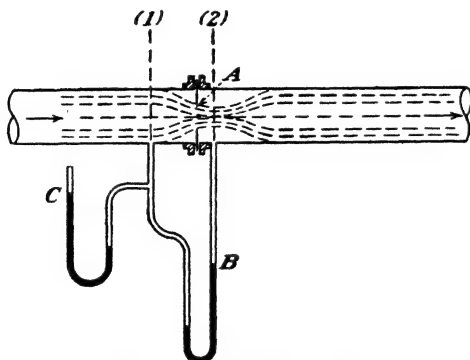
FIG. VIII.2.—Orifice meter.

The orifice, Venturi, and flow nozzle all depend on placing a constriction in the flow line so that the velocity of the fluid is momentarily increased. The increase in kinetic energy or velocity head so produced is compensated by a decrease in static-pressure head that can be measured and then related to the rate of flow. The three types mentioned differ primarily in the form of the constriction and are shown diagrammatically in Figs. VIII.2 to VIII.4. The usual type of orifice is a round hole in a thin plate with a square edge on the upstream side. The orifice is commonly placed concentrically in an ordinary pipe line between flanges, but it may also be placed in the side or the bottom of a tank and allowed to discharge to the atmosphere. The flow through the orifice causes a pressure drop, which is usually measured with a differential-pressure manometer shown at *B*. The static pressure on the upstream side of the orifice is measured by the manometer *C*. In the case of gases, the upstream temperature must also be measured.

The Venturi meter differs from the orifice in that it has a gradual approach to a section of smaller diameter, known as the "throat,"

followed by a still more gradual increase in cross section until the original
pipe diameter is again attained.
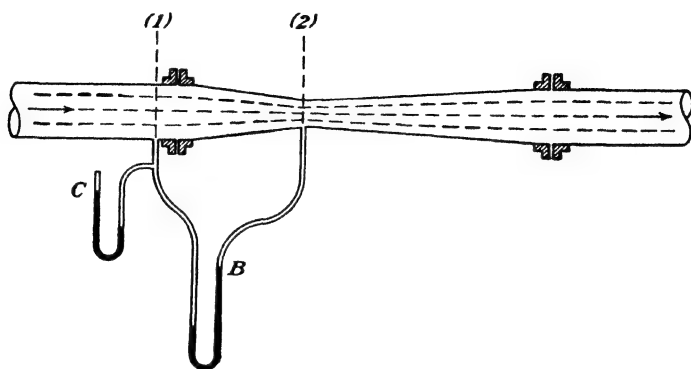
FIG. VIII.3.—Venturi meter.
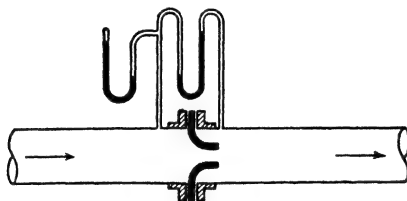
FIG. VIII.4.—Flow nozzle.

The flow nozzle is essentially an orifice with a gradual approach
as shown in Fig. VIII.4. There are many types of nozzles, but the
general principle is the same in all cases.
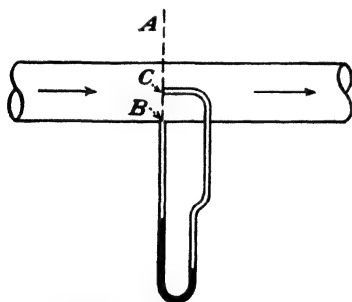
FIG. VIII.5.—Principle of the Pitot
tube.

The Pitot tube, shown diagram-
matically in Fig. VIII.5, consists of a
static-pressure opening B, whose plane
is parallel to the direction of flow, and
a kinetic-pressure opening C, whose
plane is perpendicular to the direction
of flow. The leads from both openings
will transmit the static pressure at the
plane A (the difference in elevation can
be neglected for gases, and the Pitot
tube is seldom if ever used for liquids);
but the opening C will also transmit
the pressure corresponding to the
velocity head, $u^2/2g$, so that the difference between the two, or the
differential pressure, is that due to the velocity head alone. In other

words, the Pitot tube is a means of measuring the velocity head at some particular location in the fluid stream.

Flow of Liquids in Venturi Tubes, Orifices, and Nozzles.—Since a liquid may be regarded as an incompressible fluid, the flow formulas are simpler for liquids than for gases, and we shall treat them first and then proceed to the more complex case. Our starting point will be the general equation (VIII.4); section (1) will be that at the upstream-pressure tap, and section (2) at the downstream tap (see Figs. VIII.2 and VIII.3). It will be assumed that the flow is adiabatic and frictionless and that the orifice or other differential-pressure device is not necessarily in a horizontal pipe. It is evident that $E_1 = E_2$ since the state of an incompressible fluid could not change except as a result of temperature change and this could result only from a transfer of heat or the conversion
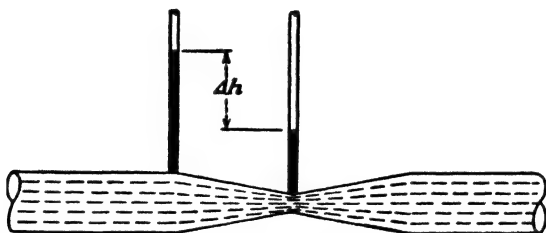
Fɪɢ. VIII.6.—Differential head.

of some mechanical energy to heat by friction. Both these possibilities are ruled out by the assumptions made. Also, since $Q = 0$, and $W_0 = 0$, Eq. (VIII.4) reduces to

$$\frac{u_2^2 - u_1^2}{2g} = p_1 v_1 - p_2 v_2 + z_1 - z_2 \qquad \text{(VIII.15)}$$

Since the fluid is incompressible, $v_1 = v_2 = v$ **and** we can transform Eq. (VIII.15) to

$$\frac{u_2^2 - u_1^2}{2g} = \frac{\Delta p}{\rho} + z_1 - z_2 = \Delta h \qquad \text{(VIII.16)}$$

$\Delta p = p_1 - p_2$ and is known as the "differential pressure." Δh is the differential head in terms of feet of the fluid flowing, or it is the vertical difference in level that would be shown by the liquid in two standpipes rising from the flow channel at sections (1) and (2) as shown in Fig. VIII.6. In the great majority of cases, $z_1 = z_2$ and $\Delta h = \Delta p/\rho$.

Equation (VIII.16) may be transformed to

$$\sqrt{u_2^2 - u_1^2} = \sqrt{2g\,\Delta h} \qquad \text{(VIII.17)}$$

Since the flow is assumed to be steady, the volume of liquid passing any

section must equal that passing any other in a given unit of time and hence we can write

$$u_1 A_1 = u_2 A_2 \qquad \text{(VIII.18)}$$

where A_1 and A_2 are the cross-sectional areas at sections (1) and (2). This equation is sometimes known as the "equation of continuity." It assumes, of course, that the flow is steady, *i.e.*, no accumulation or depletion occurs between the two sections and that both sections are completely filled with fluid.

In the case of the sharp-edged orifice, the downstream-pressure lead is placed at some distance below the orifice; and, strictly, the area A_2 should refer to the actual area of the fluid stream at this point. It is well known that the jet of fluid (whether liquid or gas) issuing from such an orifice contracts after leaving the orifice, reaches a minimum area, and then expands in area. The point of minimum area is known as the "vena contracta," and one common practice is to locate the low-pressure lead at this point. The area at this point is not readily measured, and therefore, for practical purposes, A_2 will be taken to be the area of the area of the orifice, recognizing that $A_{\text{vena contracta}} = \alpha A_2$, where α may be called a coefficient of contraction.

Now, since, for a circular pipe,

$$\frac{A_2}{A_1} = \left(\frac{D_2}{D_1}\right)^2 \qquad \text{(VIII.19)}$$

where D_1 and D_2 are the diameters of the pipe and orifice, or throat, respectively,

$$\left(\frac{u_1}{u_2}\right)^2 = \left(\frac{D_2}{D_1}\right)^4 = \beta^4 \qquad \text{(VIII.20)}$$

and then Eq. (VIII.17) can be put into the form

$$u_2 \sqrt{1 - \left(\frac{u_1}{u_2}\right)^2} = \sqrt{2g\,\Delta h} = \sqrt{2g\,\Delta(pv)} \qquad \text{(VIII.21)}$$

or

$$u_2 = \sqrt{\frac{2g\,\Delta h}{1 - \beta^4}} \qquad \text{(VIII.22)}$$

The quantity $\sqrt{1 - \beta^4}$ is frequently referred to as the "approach factor."

Actually, of course, in metering one is interested not in the velocity of flow but in the volumetric or weight rate of flow. We may write

$$u_2 = \frac{q}{A_2} = \frac{w}{\rho A_2} \qquad \text{(VIII.23)}$$

p is written without a subscript because there is no difference between the values at sections (1) and (2) for an incompressible fluid. Finally, Eq.

(VIII.22) may be written

$$q = A_2 \sqrt{\frac{2g\,\Delta h}{1 - \beta^4}} \qquad (VIII.24)$$

or

$$w = A_2 \rho \sqrt{\frac{2g\,\Delta h}{1 - \beta^4}} \qquad (VIII.25)$$

$$w = A_2 \sqrt{\frac{2g\,\rho\Delta p}{1 - \beta^4}} \qquad (VIII.26)$$

The Discharge Coefficient.—If the predictions of these theoretical equations are compared with the results of experiment, it is found that the general trend is correct, *viz.*, that the volume rate of flow does vary quite accurately as the square root of the differential head but the numerical values are not, in general, in accord with the equation. There are two main reasons for this, (1) the fact that the flow is not entirely frictionless and (2) the contraction of the jet, which occurs especially in the case of the sharp-edged orifice. The departure from theory as a result of these or any other causes is generally taken care of by the introduction of a coefficient,[1] which will be called a discharge coefficient. A discharge coefficient is defined by the equation

$$C = \frac{\text{actual discharge rate}}{\text{theoretical discharge rate}} \qquad (VIII.27)$$

and is, of course, a dimensionless quantity. The discharge rate may be expressed as weight or as volume; in the case of the latter it is obvious that the two volumes should be referred to the same conditions of state, especially if the fluid is a gas. (It should be noted that the value of C will naturally depend on the theoretical equation used to calculate the flow.) Introducing the coefficient of discharge, Eq. (VIII.24) becomes

$$q = \frac{\pi D_2^2}{4} C \sqrt{\frac{2g\,\Delta h}{1 - \beta^4}} \qquad (VIII.28)$$

and similarly for Eq. (VIII.25).

Sometimes another coefficient defined by the equation

$$q = \frac{\pi D_2^2}{4} C' \sqrt{2g\,\Delta h} \qquad (VIII.29)$$

is used, where

$$C' = \frac{C}{\sqrt{1 - \beta^4}} \qquad (VIII.30)$$

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[1] Some authorities use two coefficients, one to allow for the contraction and another to take care of all other departures from theory. We shall follow the simpler and commoner practice of combining them into one coefficient.

This coefficient is sometimes referred to as the "discharge coefficient with approach factor included." If D_2/D_1 is small, β^4 in Eq. (VIII.28) is negligible and the equation reduces to the form of Eq. (VIII.29). This is the same as neglecting u_1 in Eq. (VIII.17) and is commonly referred to as "neglecting the velocity of approach" since u_1 is the mean velocity of the fluid in the pipe above the orifice.

Illustration 3.—What is the maximum allowable value of D_2/D_1 if the velocity of approach is to be neglected without making an error of more than 1 per cent in the volume rate of discharge? Assume that flow is well into the turbulent region so that the discharge coefficient will be substantially independent of diameter ratio.

Let q_t = true rate of flow as given by Eq. (VIII.28) and q_a = approximate rate as given by Eq. (VIII.29) when C' is replaced by C.

$$\frac{q_t - q_a}{q_t} = 0.01$$

or

$$1 - \frac{q_a}{q_t} = 0.01$$

But, from Eqs. (VIII.28) and (VIII.29), $\dfrac{q_a}{q_t} = \sqrt{1 - \beta^4}$

$$\therefore \sqrt{1 - \left(\frac{D_2}{D_1}\right)^4} = 0.99$$

or

$$\left(\frac{D_2}{D_1}\right)^4 = 0.0199$$

$$\frac{D_2}{D_1} = 0.376$$

Thus we have the rule that, as long as the diameter of the orifice is three-eighths (or less) of the pipe diameter, neglect of velocity of approach will produce an error of not more than 1 per cent.

Values of the Discharge Coefficient for Liquids.—The numerical value of the coefficient C is independent of the units provided that a consistent set is used. Analysis of the problem of the dependence of C on variables leads to the conclusion that it depends on the following factors:

1. Type of meter, *i.e.*, Venturi, orifice, etc.
2. Size of the meter.
3. The rate of flow.
4. The properties of the fluid, particularly its density and viscosity.
5. Shape of the meter.

The size may be defined either by D_1 or by D_2; the rate of flow, by u, q, or w. The shape of the meter is characterized by a number of shape factors or ratios of various linear dimensions to some one dimension such as D_1. Some of the most important dimensions entering into such shape factors are

1. Lengths of approach and exit pipes.
2. Diameter of orifice, or throat.

3. Thickness of orifice plate.
4. Location of pressure leads.
5. Diameter of pressure-lead holes.
6. Roughness of pipe wall.

Factors (1), (3), (4), and (5) are generally made constant by adhering to certain specifications in the construction of a given type of meter.

Further analysis of the problem indicates that the coefficient for an instrument constructed in accordance with certain standard specifications is a function of u, μ, ρ, D_2, D_1, and β. Application of dimensional analysis then leads to the relationship

$$C = \phi(Re,\beta,D_1) \tag{VIII.31}$$

The Reynolds number is generally based on the conditions at the constriction, *i.e.*, orifice, or throat, the density and viscosity of the fluid at this point being assumed to be the same as at the upstream section. Many experiments have been made to establish the exact nature of this functional relationship, and the results have been presented both graphically and by equations. Only a few of the salient facts will be mentioned here; for further details, reference should be made to the report of the American Society of Mechanical Engineers (A.S.M.E.) Research Committee on Fluid Meters.[1]

In the case of Venturi meters, C can generally be assumed to be independent of β and D_1 within the limits commonly met in practice and to depend only on Re. In the viscous-flow region, C varies rapidly with Re, and values cannot be said to be very well established. In the turbulent region, C increases with Re from a value of about 0.90 to an asymptote of about 0.99 at very high Reynolds numbers. A value of 0.98 is probably a good average to use for most cases.

For sharp-edged orifices and turbulent flow, C is remarkably independent of the three variables in Eq. (VIII.31), and an average value of 0.605 will suffice for an accuracy of 1 to 2 per cent in the great majority of cases provided that the orifice has been carefully made and installed in accordance with standard specifications. The limiting values of C for variations of Re from 30,000 to 600,000, of β from 0.1 to 0.8, and of D_1 from 2 to 14 in. are 0.594 and 0.620. What few data there are for the viscous region indicate that C varies greatly with Re and β and values cannot be predicted with accuracy.

It may be concluded that the coefficient of discharge for a sharp-edged orifice can be accurately predicted so that calibration is unnecessary. This implies that the orifice has been carefully installed in accordance with certain specifications. The chief conditions are that

[1] "Fluid Meters—Their Theory and Application," Part 1, 4th ed., American Society of Mechanical Engineers, New York, 1937.

the orifice shall be accurately round, carefully centered in the pipe, provided with sufficient length of straight pipe both upstream and downstream and 'hat the pressure taps shall be located at definite points. For the values of the coefficients given above, the pressure leads must be either (1) flange connections or (2) throat connections. In the case of (1) the holes for the static-pressure leads are drilled into the flanges that hold the orifice plate, their centers being about 1 in. from the face of the plate. In (2) the upstream tap is located at 1 pipe diameter from the orifice and the downstream one at the vena contracta, which is about 0.5 pipe diameter from the orifice. These two types of connection give practically the same result.

Determination of the Differential Pressure.—Use of the equations just developed requires a brief con-
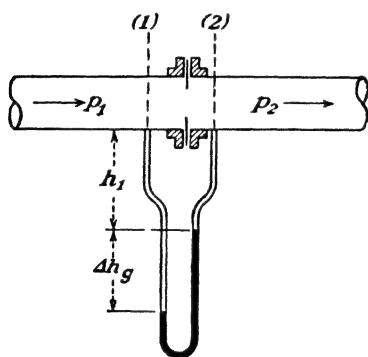
FIG. VIII.7.—Differential manometer.

sideration of the calculation of the differential pressure, or head. Thus Δh in Eq. (VIII.28), for example, generally is not read directly from the differential-pressure gauge on the meter but must be obtained by calculation. In Fig. VIII.7, the differential pressure between sections (1) and (2) is measured by a manometer filled with a fluid of higher specific gravity than the fluid flowing. The pressure leads above the gauge fluid are assumed to be filled with the fluid that is flowing in the pipe. Making a static-pressure balance when equilibrium is reached at the lower level of the gauge fluid, we have

$$p_1 + h_1\rho_f + \Delta h_g\rho_g = \Delta h_g\rho_g + h_1\rho_f + p_2$$

or

$$p_1 - p_2 = \Delta p = \Delta h_g(\rho_g - \rho_f)$$

and

$$\frac{\Delta p}{\rho_f} = \Delta h = \Delta h_g \left(\frac{\rho_g}{\rho_f} - 1\right) \qquad \text{(VIII.32)}$$

Δh is the differential head in terms of the fluid flowing, ρ_g the density of the manometer fluid, and ρ_f the density of the flowing fluid.

Regain of Pressure.—The sharp-edged orifice is a much simpler and cheaper device than a Venturi tube, but the latter possesses an important advantage in that the permanent pressure drop caused by it is considerably less than in the case of the orifice. In the orifice the sudden enlargement in cross section from that of the orifice to that of the pipe results in the dissipation of much of the kinetic energy by conversion to heat, whereas in the Venturi the gradual increase in cross section from the throat causes a conversion of the kinetic energy to the mechanical

energy represented by the term pv. The percentage of the original upstream pressure that is lost depends on a number of circumstances; but in a well-made Venturi, under normal conditions, approximately 80 to 90 per cent of the differential-pressure reading is regained, whereas in an orifice the regain is only 5 to 50 per cent, depending on the ratio of orifice to pipe diameter. The permanent loss in head for a flow nozzle is intermediate between that for the Venturi and the sharp-edged orifice.

Discharge from a Tank with Varying Head.—In the case of a tank of liquid discharging through an orifice in the side or the bottom into the air, the general equation (VIII.24) can be written

$$q = \frac{dV}{d\theta} = \frac{\pi D_2^2}{4} C \sqrt{2gh} \qquad \text{(VIII.33)}$$

where h is the instantaneous head above the center of the orifice and $dV/d\theta$ is the rate of discharge at the same instant. Now, since

$$dV = A \, dh$$

where A = mean cross section of the tank, Eq. (VIII.33) becomes

$$A \frac{dh}{d\theta} = \frac{\pi D_2^2}{4} C \sqrt{2gh} \qquad \text{(VIII.34)}$$

Assuming A to be constant,

$$\frac{dh}{h^{\frac{1}{2}}} = K\theta \qquad \text{(VIII.35)}$$

where

$$K = \frac{\pi D_2^2 C \sqrt{2g}}{4A}$$

Integrating Eq. (VIII.35) between limits h_1 at $\theta = 0$ and h_2 at $\theta = \theta$,

$$h_1^{\frac{1}{2}} - h_2^{\frac{1}{2}} = \frac{K}{2} \theta \qquad \text{(VIII.36)}$$

The lower limit of h should be chosen at some value greater than zero because the orifice equation ceases to hold at very low heads and there are also difficulties due to vortex formation and to effects of surface tension.

Since $V = A(h_1 - h_2)$, Eq. (VIII.36) becomes

$$V = \frac{\pi D_2^2 C \sqrt{2gh_1}}{4} \theta - \frac{\pi^2 D_2^4 C^2 g \theta^2}{32A} \qquad \text{(VIII.37)}$$

Equation (VIII.36) can also be written

$$V = \frac{\pi D_2^2 C \sqrt{2g}}{4} \theta \left(\frac{\sqrt{h_1} + \sqrt{h_2}}{2} \right) \qquad \text{(VIII.38)}$$

or
$$V = \frac{\pi D_2^2 \theta C \sqrt{2gh_{av}}}{4}$$

where $h_{av} = (h_1 + 2\sqrt{h_1 h_2} + h_2)/4$.

Aside from any fluid-flow application this equation is interesting because it introduces the student to a type of average other than the very common arithmetic and logarithmic means.

The value of C for an orifice discharging liquid into a gas space is not so well established as for the usual case of a submerged orifice, but for a sharp-edged orifice in a thin plate the value of 0.60 should be a good approximation. For a short tube acting as the orifice (ratio of length to diameter about 3) $C = 0.80$ approx.[1]

GAS-FLOW MEASUREMENT

General Theoretical Equations.—The same general principles apply as in the case of the metering of liquids, but there are some important differences that need to be taken into account. These result from the fact that the fluid is compressible and changes its volume rapidly with changes in conditions. Consequently, its pressure and temperature must be determined in order to fix the density (in the case of wet vapors, the quality must be known); furthermore, if the pressure differential is a significant fraction of the absolute pressure, there will be a change in density in the meter itself that must be taken into account for accurate results.

Going back to the general equation (VIII.4) based on the first law of thermodynamics, we shall still assume adiabatic conditions and, of course, $W_0 = 0$. We may also assume $z_1 = z_2$ since the difference in gravity heads for a gas is almost always very small. With these assumptions, Eq. (VIII.4) becomes[2]

$$\frac{u_2^2 - u_1^2}{2g} = J(E_1 - E_2) + p_1 v_1 - p_2 v_2 = J(H_1 - H_2) \quad \text{(VIII.39)}$$

As before, subscripts 1 and 2 refer to the sections at which the pressure taps are located with the exception, already noted, in the case of a sharp-edged orifice that A_2 refers to the area of the orifice itself.

Now, since the mass rate of the fluid is constant,

$$w = u_1 A_1 \rho_1 = u_2 A_2 \rho_2 \qquad \text{(VIII.40)}$$

or
$$\frac{u_1}{u_2} = \frac{A_2}{A_1} \frac{\rho_2}{\rho_1} = \left(\frac{D_2}{D_1}\right)^2 \frac{\rho_2}{\rho_1} \qquad \text{(VIII.41)}$$

[1] BOSTON, O. W., *Chem. Met. Eng.*, **30**, 56–59 (1924).
[2] J is explicitly shown in this case to avoid confusion in the subsequent treatment.

Substituting Eq. (VIII.41) in (VIII.39) and rearranging,

$$u_2 = \sqrt{\frac{2gJ \, \Delta H}{1 - \beta^4 \left(\dfrac{\rho_2}{\rho_1}\right)^2}} \qquad \text{(VIII.42)}^*$$

If D_2/D_1 is small (0.4 or less), Eq. (VIII.42) reduces to

$$u_2 = \sqrt{2gJ \, \Delta H} \qquad \text{(VIII.43)}$$

The theoretical volume or weight discharged is obtained by combining Eq. (VIII.42) with the equations

$$q_2 = u_2 A_2$$

or

$$w = u_2 A_2 \rho_2$$

Thus the mass-flow equation is

$$w = A_2 \rho_2 \sqrt{\frac{2gJ \, \Delta H}{1 - \beta^4 \left(\dfrac{\rho_2}{\rho_1}\right)^2}} \qquad \text{(VIII.44)}$$

In using this equation, H_1 could be read directly from a table of thermodynamic properties and H_2 could be similarly obtained after making the assumption that the fluid expanded isentropically from p_1 to p_2.

Special Case of Ideal Gas.—If the fluid is an ideal gas, $(\partial H/\partial p)_T = 0$ and

$$\begin{aligned}
\Delta H &= \int C_p \, dT \\
&= \int \frac{kR}{M(k-1)} \, dT \\
&= \frac{kR}{M(k-1)} (T_1 - T_2) \qquad \text{(VIII.45)}
\end{aligned}$$

but since, for an isentropic expansion of an ideal gas,

$$T_2 = T_1 \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} \qquad \text{(VII.23)}$$

we can write

$$\Delta H = \frac{kRT_1}{M(k-1)} \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right] \qquad \text{(VIII.46)}$$

Substituting Eq. (VIII.46) in Eq. (VIII.43),

$$u_2 = \sqrt{\frac{2gJkRT_1}{M(k-1)} \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]} \qquad \text{(VIII.47)}$$

or since

$$RT_1 = \frac{Mp_1 v_1}{J}$$

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* Note that ΔH in this treatment $= H_1 - H_2$ and is based on 1 lb. mass.

when R is in thermal units, Eq. (VIII.47) can be transformed to

$$u_2 = \sqrt{\frac{2gkp_1v_1}{k-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]} \qquad \text{(VIII.48)}$$

or if the approach factor is not negligible,

$$u_2 = \sqrt{\frac{2gkp_1v_1[1 - (p_2/p_1)^{\frac{k-1}{k}}]}{(k-1)[1 - \beta^4(\rho_2/\rho_1)^2]}} \qquad \text{(VIII.49)}$$

The weight-discharge equation corresponding to Eq. (VIII.49) becomes, when use is made of the fact that

$$p_1v_1^k = p_2v_2^k \qquad \text{(VII.15)}$$

and

$$\therefore \frac{\rho_2}{\rho_1} = \left(\frac{p_2}{p_1}\right)^{\frac{1}{k}}$$

$$w = A_2\rho_1 r^{\frac{1}{k}} \sqrt{\frac{[2gkp_1v_1/(k-1)](1 - r^{\frac{k-1}{k}})}{1 - \beta^4(r)^{\frac{2}{k}}}} \qquad \text{(VIII.50)}$$

$$w = A_2 \sqrt{\frac{[2gkp_1\rho_1/(k-1)]r^{\frac{2}{k}}(1 - r^{\frac{k-1}{k}})}{1 - \beta^4(r)^{\frac{2}{k}}}} \qquad \text{(VIII.51)}$$

where $r = p_2/p_1$. Equations (VIII.50) and (VIII.51) give the theoretical discharge rate and must be modified by empirical coefficients to give the actual rate just as in the case of liquid flow. The particular coefficient for use with these equations will be designated as C_a the adiabatic-discharge coefficient. Experiment shows that, for Venturi meters, nozzles, rounded orifices, and other devices in which the minimum cross section of the fluid jet is confined in a definite channel, C_a is substantially constant and its value is not far from unity in most cases. This is not true, however, for the sharp-edged orifice, for which C_a varies considerably with pressure ratio r.

Reduction to the Simple Hydraulic Formula.—Let $p_2 = p_1 - \Delta p$ and therefore $p_2/p_1 = 1 - (\Delta p/p_1)$. Expanding by the binomial theorem, we have

$$\left(1 - \frac{\Delta p}{p_1}\right)^{\frac{k-1}{k}} = 1 - \frac{k-1}{k}\frac{\Delta p}{p_1} + \frac{k-1}{2k}\left(-\frac{1}{k}\right)\left(\frac{\Delta p}{p_1}\right)^2 + \cdots$$

At the limit where $\Delta p \to 0$, this reduces to

$$1 - \frac{k-1}{k}\frac{\Delta p}{p_1}$$

and therefore the term $1 - (p_2/p_1)^{\frac{k-1}{k}}$ in Eq. (VIII.48) reduces, when the pressure drop Δp is very small, to

$$\frac{k-1}{k}\frac{\Delta p}{p_1}$$

Substituting this in Eq. (VIII.48) gives

$$u_2 = \sqrt{2g\,v_1\Delta p} \qquad\qquad (VIII.52)$$

or, putting in the correction for velocity of approach and dropping the subscript on v since the density does not change for this limiting case,

$$u_2 = \sqrt{\frac{2gv\,\Delta p}{1-\beta^4}} \qquad\qquad (VIII.53)$$

or, since $w = u_2 A_2\rho$,

$$w = A_2\sqrt{\frac{2g\rho\,\Delta p}{1-\beta^4}} \qquad\qquad (VIII.54)$$

Equations (VIII.52) to (VIII.54) are the same as the ones already derived for liquids. Since they are based on the assumption that Δp is very small and therefore that the change in density of the gas is substantially negligible, they could have been derived directly from Bernoulli's theorem just as Eq. (VIII.22) was.[1] This amounts to making the assumption that the density of the gas does not change or that it behaves substantially as a liquid. Furthermore, since Eq. (VIII.52) or (VIII.54) is strictly true only when $\Delta p \to 0$ and hence density is constant, it is immaterial from a theoretical viewpoint whether one uses for v the upstream specific volume, the downstream specific volume, or an average. There is a practical advantage in the use of an average, as will be shown later (page 330). Since in most cases, there will be a small but significant difference between these three densities, the value of the empirical discharge coefficient C to be used with Eq. (VIII.54) will depend on which density is chosen. In giving values of C one should be careful to note which one was used.

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[1] An alternative derivation is as follows:

$$dH = \frac{v\,dp}{J} + T\,dS \qquad\qquad (III.89)$$

For an isentropic expansion, $\qquad \Delta H = \frac{1}{J}\int v\,dp$

$$= \frac{v\,\Delta p}{J}$$

if volume change can be neglected.

Substitution in Eq. (VIII.43) gives Eq. (VIII.52). Note that Eq. (VIII.52) does not involve the assumption of an ideal gas.

By retaining the square term as well as the first-power term of the expansion, an equation is obtained that is somewhat simpler than Eq. (VIII.48) and yet is quite accurate as long as p_2/p_1 is greater than 0.75.

The Expansion Factor.—The general equation (VIII.51) is sometimes put in the form of the simple hydraulic equation as follows:

$$w = A_2 Y_1 \sqrt{\frac{2g\rho_1 \, \Delta p}{1 - \beta^4}} \qquad \text{(VIII.55)}$$

where Y_1 is an expansion factor based on upstream density whose value is seen to be [from Eqs. (VIII.55) and (VIII.51)]

$$Y_1 = \sqrt{\frac{[k/(k-1)](r)^{\frac{2}{k}}[1 - (r)^{\frac{k-1}{k}}](1 - \beta^4)}{[1 - \beta^4(r)^{\frac{2}{k}}](1 - r)}} \qquad \text{(VIII.56)}$$

If β is less than 0.35, the terms involving this ratio may be omitted without affecting the value of Y by more than 1 per cent. The expansion factor could also be based on the use of the downstream density or the mean density in Eq. (VIII.55). It is easy to show that the following relations hold between these various factors:

$$Y_2 \text{ (factor based on } \rho_2) = \frac{Y_1}{\sqrt{r}} \qquad \text{(VIII.57)}$$

and $\qquad Y_m$ (factor based on mean density) $= Y_1 \sqrt{\dfrac{2}{1 + r}}$ (VIII.58)

The expansion factor depends primarily on (1) the specific-heat ratio k, (2) the diameter ratio β, and (3) the pressure ratio r. Dimensional analysis indicates that it may be expressed as a function of the two dimensionless ratios $\Delta p/p_1 k$ (sometimes called the "acoustic ratio") and β, and this has been confirmed by experiment.[1]

Working Equations for Practical Use.—To take care of frictional effects and other departures from the ideal conditions assumed in their derivation, the equations for gas flow must also include a discharge coefficient to be determined empirically. We have already defined a coefficient C_a for use with Eq. (VIII.51) that is known as the adiabatic-discharge coefficient. Equation (VIII.55) may be written

$$w = C_0 A_2 Y_1 \sqrt{\frac{2g\rho_1 \, \Delta p}{1 - \beta^4}} \qquad \text{(VIII.59)}$$

where C_0 is the hydraulic discharge coefficient, *i.e.*, the coefficient that would be measured experimentally when Y_1 approaches 1.0. **This may**

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[1] SMITH, E. S., JR., *Trans. A.S.M.E.*, **52**, HYD-52-7b, 89–109 (1930).

be regarded as a universal equation for any case of flow through a head meter. It involves the two empirical factors C_0 and Y_1, which, in general, must be related to the flow conditions by test data. They are best treated separately rather than by combining them into a single factor because they depend on different things. C_0, as we have seen, depends on D_1, Re, and β while Y_1 depends on $\Delta p/kp_1$ and β.

Equation (VIII.59) may be put in the more immediately useful form

$$w = 0.525 C_0 D_2^2 Y_1 \sqrt{\frac{\rho_1 \Delta p}{1 - \beta^4}} \qquad \text{(VIII.60)}$$

where w = flow rate, lb. per sec.

D_2 = diameter of orifice, or throat, in.

Δp = pressure differential, lb. per sq. in.

ρ_1 = upstream fluid density, lb. per cu. ft.

Since C_0 is a function not of the individual fluid properties but of the Reynolds number, it will have the values already given for the case of liquids regardless of the fluid being metered. A value of 0.605 is a good average value for a square-edged orifice in many cases.

Values of Y_1 for Venturi tubes, nozzles, and rounded orifices can be calculated with sufficient accuracy from Eq. (VIII.56), but for sharp-edged orifices the values must be determined by experiment. This difference arises from the fact that the expansion of a gas in a sharp-edged orifice is a more complex phenomenon than expansion in a Venturi or nozzle owing to the distortion of the flow lines caused by the orifice. With a gas there is a vena contracta just as in the case of liquids; but whereas the ratio of the jet area at the point of greatest contraction to the orifice area is substantially a constant in the case of liquids, it is undoubtedly variable in the case of gases and dependent on the pressure ratio and other factors.

Figure VIII.8 presents in graphical form values of Y_1 calculated from Eq. (VIII.56) for Venturis, nozzles, and rounded orifices as a function of k, r, and β. In the case of square-edged orifices with throat connections, Buckingham[1] found the following equation,

$$Y_1 = 1 - \frac{\Delta p}{kp_1} (0.41 + 0.35\beta^4) \qquad \text{(VIII.61)}$$

to apply within the limits of $\beta = 0.20$ to 0.75.

As a result of their extensive tests on the flow of air through sharp-edged orifices, workers at the Bureau of Standards[2] found that the use of a mean density (density at upstream temperature and arithmetic

[1] BUCKINGHAM, E., *Bur. Standards J. Research*, **9**, 61–79 (1932).

[2] BEAN, H. S., E. BUCKINGHAM, and P. S. MURPHY, *Bur. Standards J. Research*, **2**, 562–658 (1929).

average of upstream and downstream pressures) in the simple hydraulic equation resulted in a discharge coefficient which varied only a few per cent from the coefficient for water over the whole range from $r = 1$ down to $r = 0.50$.   This coefficient is defined by the equation

$$w = 0.525 C_m D_2^2 \sqrt{\frac{\rho_m \, \Delta p}{1 - \beta^4}} \qquad \text{(VIII.62)}$$

Figure VIII.9 taken from the above-mentioned paper shows the variation of C_m, C_a, and C_0 (based both on upstream and on downstream density)
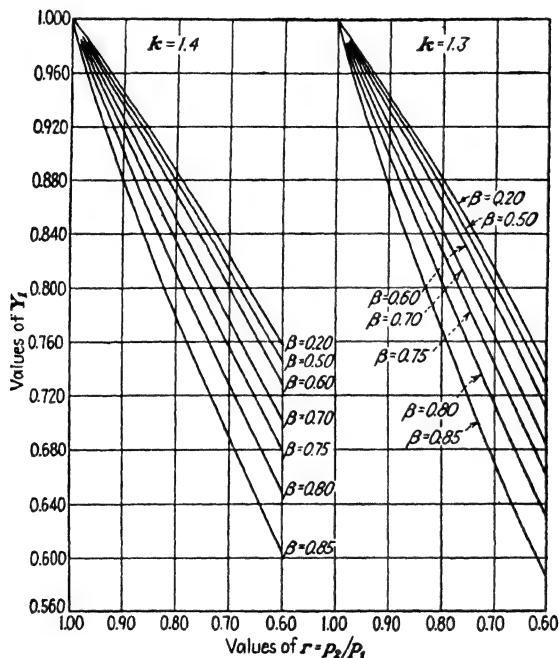
Fig. VIII.8.—Values of the expansion factor, Y_1, for Venturi meters, nozzles, and rounded orifices.   (*Reproduced, with permission, from "Fluid Meters—Their Theory and Application," Part I, 4th ed., American Society of Mechanical Engineers.*)

with r for the case where $\beta \to 0$.* Naturally, all three coefficients approach a common value, 0.597 in this case, as $r \to 1.0$.   It is of interest to note that C_a varies even more than C_0.   It would appear that Eq. (VIII.62) with C_m equal to 0.600 can be used as a universal equation for all fluids flowing through sharp-edged orifices with throat taps provided

* For this case the value of the coefficient is independent of the location of the pressure taps.   For larger values of β, C_m is still nearly independent of r but depends on the location of the taps.

that an accuracy of 2 per cent is sufficient. In the case of gases it should also be restricted to cases where the pressure ratio is greater than the critical value. Molstad and Varga[1] give a nomograph to facilitate the solution of this equation.

Since
$$\rho_m = \frac{M(p_1 + p_2)}{2RT_1}$$

for the case of ideal gases, Eq. (VIII.62) can also be put in the form

$$w = 0.1133 C_m D_2^2 \sqrt{\frac{M(p_1^2 - p_2^2)}{T_1}} \qquad (\text{VIII.63})$$

when T_1 is in degrees Rankine and the other units are the same as in Eq. (VIII.60).
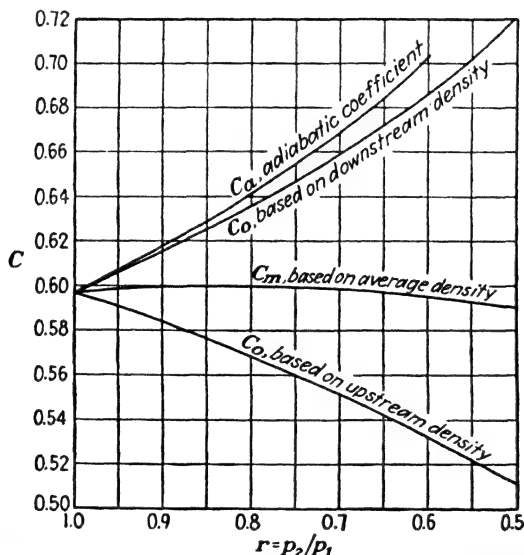
Fig. VIII.9.—Variation of discharge coefficients for a sharp-edge orifice, with the pressure ratio when $\beta \rightarrow 0$. [*Reproduced, with permission, from Bur. Standards J. Research,* **2**, 562–658 (1929).]

Maximum Discharge and the Critical Ratio.—The gas-flow equations that have been developed in the previous sections are valid only when the pressure ratio is above a certain critical value, which we shall next proceed to determine.

For a given gas and given upstream conditions and for the case where the velocity of approach may be neglected (denominator under the radical reduces to unity), Eq. (VIII.51) can be written in the following

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[1] MOLSTAD, M. C., and F. B. VARGA, *Chem. Met. Eng.*, **44**, 143 (1937).

simplified form:

$$w^2 = K[r^{\frac{2}{k}} - r^{\frac{k+1}{k}}] \qquad \text{(VIII.64)}$$

where K is a constant, assumed independent of r or w. Inspection of this equation shows that $w = 0$ both when $p_1 = p_2$ ($r = 1$) and when $p_2 = 0$ ($r = 0$), or with discharge into a vacuum. Let us now inquire how w changes as r is decreased from the limiting value of 1.0. w will naturally increase at first, but it would not be expected to do so indefinitely. Actually, it is found that w increases to a maximum when a certain value of r, known as the "critical ratio" and designated by r_c, is reached. This may be predicted from the equation by the usual method of the differential calculus.

Differentiation of Eq. (VIII.64) yields

$$2w\frac{dw}{dr} = K\left[\frac{2}{k}r^{\frac{2}{k}-1} - \frac{k+1}{k}r^{\frac{1}{k}}\right] \qquad \text{(VIII.65)}$$

Putting $dw/dr = 0$ and solving for r, one has

$$r_c = \left(\frac{2}{1+k}\right)^{\frac{k}{k-1}} \qquad \text{(VIII.66)}$$

Substituting this value of r in Eq. (VIII.48) and eliminating p_1v_1 by the adiabatic-expansion equation in the form

$$p_1v_1 = p_2v_2(r)^{\frac{1-k}{k}} \qquad \text{(VIII.67)}$$

one gets

$$u_{2(max)} = \sqrt{gkp_2v_2} \qquad \text{(VIII.68)}$$

This is the well-known equation for the velocity of sound in an ideal gas. That such a result should be obtained seems entirely reasonable though no less remarkable that it should be so simply predicted from the application of thermodynamics. It is to be expected since the acoustical velocity represents the maximum speed at which a pressure effect could be propagated through a gas. As the pressure on the downstream side of an orifice or nozzle is reduced, the velocity in the throat increases until the critical pressure is reached at which the velocity under the throat conditions is equal to the velocity of sound. Any further reduction in pressure in the downstream chamber would have no effect on the throat pressure, which would remain at the critical value. (Note, however, that velocities higher than the velocity of sound are obtained in expanding nozzles.)

Values of the critical pressure ratio, computed from Eq. (VIII.66), at 15°C. are 0.49 for monatomic gases, 0.53 for diatomic gases, and slightly higher for gases of greater atomic complexity. For moderately

superheated steam, r_c may be assumed to be 0.55 and for saturated steam 0.58.

If r is always taken to be the ratio of the pressure at the throat to the upstream pressure, Eq. (VIII.51) and related equations will give the correct result. One is apt to think, however, of the expansion taking place from a given upstream pressure p_1 to a final downstream pressure p_2, and the use of this ratio would be erroneous if p_2/p_1 were less than r_c. Consequently, it is better to consider Eq. (VIII.51) as applying only when p_2/p_1 is equal to or greater than the critical value. When p_2/p_1 is less than the critical value, substitute for r in Eq. (VIII.51) the critical value [Eq. (VIII.66)] and obtain the equation (neglecting the correction term for velocity of approach and adding the discharge coefficient)

$$w = C_a A_2 \sqrt{gk p_1 \rho_1 \left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}} \qquad \text{(VIII.69)}$$

or, eliminating $p_1 \rho_1$,

$$w = C_a A_2 p_1 \sqrt{\frac{gkM}{RT_1} \left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}} \qquad \text{(VIII.70)}$$

Equations (VIII.69) and (VIII.70) should be used whenever p_2, whether measured or assumed, is less than $r_c p_1$. It should be noted that the critical phenomena are observed in rounded orifices and nozzles but not in square-edged orifices. With the latter type of orifice the flow continues to increase as the pressure ratio is lowered below the value given by Eq. (VIII.66). However, very little work has been done with square-edged orifices under these conditions so that only a general statement can be made.

Nonideal Gases.—All equations after Eq. (VIII.44) are based on the assumption of ideal gases. If the departure from ideality is appreciable, it is believed that reasonably accurate results can still be obtained from these equations if the actual density is used for $\rho_1 (= 1/v_1)$. This is certainly the case if Δp is a small fraction of p_1 and the simple hydraulic formula (VIII.54) applies. The accuracy of the procedure is open to some doubt when the expansion factor Y departs appreciably from unity, but at least it should serve as a first approximation. Methods for calculating the densities of gases that cannot be assumed ideal were given in Chap. V.

Effect of Changes in State on Gas-flow Measurement.—For the present discussion it will be assumed that the simple hydraulic equation is applicable either with the upstream density as in Eq. (VIII.59) with $Y_1 = 1.00$ or with the average density as in Eq. (VIII.62). For a given

meter installation (orifice, Venturi, or nozzle) we can write

$$w = C_M \sqrt{\rho \, \Delta p} \qquad \text{(VIII.71)}$$

where C_M is a meter constant that can be determined once and for all and that is, within the limits usually encountered in any practical case, independent of w, Δp, or ρ. C_M is determined either by calibration or more commonly by calculation from the known dimensions and known values of C_0 under the mean conditions at the instrument. Using Eq. (VIII.59) its value is

$$C_M = C_0 A_2 \sqrt{\frac{2g}{1 - \beta^4}} \qquad \text{(VIII.72)}$$

The flow is calculated by Eq. (VIII.71) from the indicated or recorded values of Δp and from a value of ρ that is obtained from the observed pressure and temperature, the properties of the metered gas being known. For a direct-reading meter, the equation is

$$w = C_M' \sqrt{\Delta p} \qquad \text{(VIII.73)}$$

and since C_M' involves the density, the meter reads correctly for only one state of the gas and a correction factor must be applied for all other states. We shall now consider how the corrections may be most easily made.

The density of the gas may change as a result of change in (1) temperature, (2) pressure, (3) composition of dry gas, and (4) moisture content. Assuming the ideal-gas law,

$$\rho = \frac{pM}{RT}$$

If p and t are the upstream absolute pressure and the temperature in degrees Fahrenheit, respectively, and if M_D is the molecular weight of the dry gas and x the mole fraction of water vapor, we have

$$\rho = \frac{p[M_D(1 - x) + 18x]}{R(t + 459.7)} \qquad \text{(VIII.74)}$$

and C_M' for a given upstream condition can be calculated from Eqs. (VIII.72) and (VIII.74).

Let subscript 0 represent the upstream conditions for which the constant C_M' is known, and let the symbols without subscript represent any different set of conditions. Using absolute pressures and temperatures and the molecular weight of the moist gas to simplify the writing of the equation, we can write

$$\frac{\rho}{\rho_0} = \frac{p}{p_0} \frac{T_0}{T} \frac{M}{M_0} \qquad \text{(VIII.75)}$$

If w_0 is the weight of gas flowing through a given meter when the density was ρ_0, then, for another condition, w, the weight flowing for the same meter reading will be given by

$$w = w_0 \sqrt{\frac{p}{p_0}} \sqrt{\frac{T_0}{T}} \sqrt{\frac{M}{M_0}} \qquad \text{(VIII.76)}$$

or $\qquad\qquad w = w_0 f_p \times f_T \times f_M \qquad\qquad$ (VIII.77)

Values of these correction factors can be plotted or tabulated over the range of variation likely to be encountered in any given case so that the correction can be made with the least trouble.

The flow may be desired in terms of volume rather than weight. Using subscript s for the standard conditions of p and T to which the volume is referred,

$$w = q_s \rho_s$$

and $\qquad\qquad \rho_s = \dfrac{p_s M}{R T_s}$

Substituting in Eq. (VIII.71),

$$q_s = C_M \left(\frac{T_s}{p_s} \right) \sqrt{\frac{R p \, \Delta p}{M T}} \qquad \text{(VIII.78)}$$

For a given meter and given set of upstream conditions and given reference state, this reduces to

$$q_s = C_M'' \sqrt{\Delta p} \qquad \text{(VIII.79)}$$

For a given set of conditions, C_M'' like C_M' would be known either through direct calibration or by calculation. If the state of the gas above the orifice or Venturi changes from p_0, T_0, and M_0 for which the coefficient C_M'' applies, then by Eq. (VIII.78)

$$q_s = q_{s_0} \sqrt{\frac{p}{p_0}} \sqrt{\frac{T_0}{T}} \sqrt{\frac{M_0}{M}} \qquad \text{(VIII.80)}$$

Note that the correction factor for composition is reversed from what it was in the case of correcting a weight flow.

It should be noted that, if the gas being metered is wet or is a pure vapor, it might not exist wholly as a gas at the chosen standard state. In other words, partial or total condensation might occur if the gas were actually reduced to the standard state. It is customary to ignore this and use a fictitious standard volume based on the assumption of no condensation.

In the laboratory an orifice is frequently calibrated by measuring the discharge volume for a given set of conditions and plotting the volume against the square root of the manometer reading or directly against it on log-log paper. The volume read from the graph must then be cor-

rected for changes in pressure, temperature, or specific gravity from those that held during the calibration. A better procedure is the following one: Equation (VIII.71) can be put in the form

$$q = C_M \sqrt{\frac{TR_m}{pM}} \qquad \text{(VIII.81)}$$

where q is volume at the orifice conditions, C_M is the meter constant, and R_m is the reading of a differential-pressure gauge. As pointed out by Whitwell,[1] it is advantageous to plot $q \sqrt{pM/T}$ vs. $\sqrt{R_m}$ and then the correction for changing conditions will not be overlooked and it will be made correctly without the necessity of thinking about it.

THE PITOT TUBE

This is the simplest of all the head meters from a theoretical standpoint. But since it has features that differentiate it markedly from the other types of head meter, we have chosen to treat it separately.

The general equation for the Pitot tube would be obtained from the general energy equation (VIII.5) by letting Q and $W_0 = 0$. In this case subscript 1 refers to conditions in the undisturbed stream near the impact tube and 2 refers to conditions in the mouth of this tube. u_1 has a special significance in that it is not the average velocity of the whole stream but only the average velocity of the fluid in the small cylinder intercepted by the impact tube. At the limit where the impact opening approaches zero, the velocity would be the local velocity at a point. Since there is no flow in the impact tube, $u_2 = 0$, and the equation becomes

$$u_1 = \sqrt{2g(\Delta H + \Delta z)} \qquad \text{(VIII.82)}$$

Except in unusual cases of very high velocity, the compression due to the impact, even in the case of gas flow, will be negligible, and the equation reduces to

$$u_1 = \sqrt{2g \frac{\Delta p}{\rho} + \Delta z} \qquad \text{(VIII.83)}$$

and if the difference in gravity head is neglected, we obtain

$$u_1 = \sqrt{2g \frac{\Delta p}{\rho}} = \sqrt{2g \, \Delta h} \qquad \text{(VIII.84)}$$

the equation usually given for the Pitot tube. As this equation shows, the Pitot tube is essentially a device for measuring velocity head at a given small area in the cross section of the stream. Introducing a coefficient to allow for departure from theory due to disturbances in the

[1] WHITWELL, J. C., *Ind. Eng. Chem.*, **30**, 1157–1161 (1938).

flow caused by the tube itself or by fittings or bends in the line or other causes, we have

$$u = C_t \sqrt{2g \, \Delta h} \qquad \text{(VIII.85)}$$

or if the velocity head is measured by a head of gauge fluid of density ρ_g, we have, by Eq. (VIII.32),

$$u = C_t \sqrt{2g \, \Delta h_g \left(\frac{\rho_g}{\rho_f} - 1 \right)} \qquad \text{(VIII.86)}$$

or, for mass flow in a circular pipe,

$$w = \frac{\pi \, D^2 \rho_f}{4} \, C_t \sqrt{2g \, \Delta h_g \left(\frac{\rho_g}{\rho_f} - 1 \right)} \qquad \text{(VIII.87)}$$

where D is the diameter of the pipe.

The coefficient C_t will depend somewhat on the design of the tube but is generally considered to be close to unity for a properly made tube.

It has been noted that the Pitot tube measures the velocity of the fluid at one small element of the cross-sectional area. In order to determine the mass or volume flow for the whole channel it is customary to proceed in either of two ways: (1) Place the impact pressure tube in the center of the pipe where the velocity is a maximum, and from this maximum velocity (u_{max}) obtain the average velocity (u_{av}) from a previously determined relationship between them. (2) Use a movable impact tube and measure the velocity at a number of points across the diameter corresponding to equal areas, and take the arithmetic mean of the individual velocities.

The ratio u_{av}/u_{max} has been shown by dimensional analysis to be a function of the Reynolds number, $Du\rho/\mu$; and, for a normal velocity distribution such as would obtain in a straight run of pipe with no fittings or obstructions for at least 50 diameters on the upstream side, the functional relationship is shown in Fig. VIII.10. This is purely empirical except for the viscous region ($Re < 2,100$) where the value 0.50 may be obtained from theory. When the flow is well in the turbulent region, an average value of $u_{av}/u_{max} = 0.80$ is sufficiently accurate for most purposes.

The Pitot tube is seldom used for commercial metering because of its doubtful accuracy, but it is very convenient in experimental or testing work where high accuracy is not required. Its great advantage lies in its cheapness and in the fact that it can be inserted into any pipe line without disturbing the flow or making any changes in the line.

A disadvantage of the Pitot tube is the small reading obtained with gases under ordinary circumstances and the resultant necessity for a sensitive manometer, which is unsatisfactory under plant conditions.

Illustration 4.—What reading in inches of water would be given by a Pitot tube inserted at the center of a length of straight pipe conveying air at 70°F., 1 lb. per sq. in. gauge above normal barometer, and at an average velocity of 10 ft. per sec.? Assume $u_{av}/u_{max} = 0.80$ and $C_t = 1.00$.

By Eq. (VIII.85),
$$\frac{10}{0.80} = \sqrt{64.4\,\Delta h}$$

$$\Delta h = 2.43 \text{ ft. of air} = \Delta h g \left(\frac{\rho_g}{\rho_f} - 1\right)$$

$$\rho_f = \frac{29}{359} \times \frac{492}{530} \times \frac{15.7}{14.7} = 0.0800 \text{lb./cu. ft.}$$

$$\Delta h_g \text{ (in. H}_2\text{O)} = \frac{12 \times 2.43}{(62.4/0.0800) - 1} = 0.0373$$

The reading increases with the square of the velocity and as the first power of the gas density. Thus, hydrogen would give a very small read-
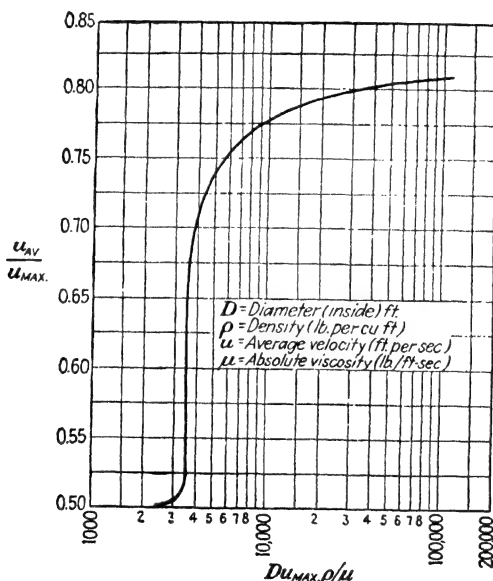
Fɪɢ. VIII.10.—Ratio of average to maximum velocity in circular pipes.

ing unless the velocity were abnormally high. The reading of a Pitot can be increased by substituting for the static-pressure tube a tube in the same axial plane as the impact tube, but facing downstream. This is sometimes known as the "reversed-tube type." Little is known about the coefficient for such a meter, and it must be calibrated under the actual conditions. The reading is never twice that obtained with the ordinary Pitot but of the order of 40 per cent greater.

NUMERICAL ILLUSTRATIONS OF USE OF FLOW EQUATIONS

Application of some of the equations developed will be illustrated by a series of numerical examples. In using the equations it should be noted that consistent units must be employed; otherwise, the coefficients will not be pure numbers, and their values will vary with the units. Thus in using Eq. (VIII.59), a consistent set of units would be A_2 in square feet, g in feet per second per second, Δp in pounds per square foot, and ρ in pounds per cubic foot. This will give w in lbs. per second. In an equation like Eq. (VIII.78) [combined with Eq. (VIII.72)] the same units for A_2, g, and Δp combined with a value of R involving v in cubic feet will give q_s in cubic feet per second. Note, however, that p and T can be in any units desired as long as the proper value of R is used.

Illustration 5.—A square-edged orifice in a thin plate has been calibrated with dry air at 70°F. and substantially standard atmospheric pressure and a plot prepared from which the volume of air per minute referred to 32°F. and standard barometer may be read directly. If this meter were used to measure the flow of dry CO_2 gas at 70°F. and atmospheric pressure, also referred to the same standard conditions, would it give low or high results? State the correction factor to be used.

Since CO_2 has a greater density than air, it is clear that a smaller flow of CO_2 than air will suffice for the same gauge reading. Therefore, the meter will read high when used with CO_2.

From Eq. (VIII.80),
$$q_s(CO_2) = q_s \text{ (air) } \sqrt{\frac{M_{air}}{M_{CO_2}}}$$
$$= q_s \text{ (air) } \sqrt{\tfrac{29}{44}} = 0.812 q_s \text{ (air)}$$

To obtain the volume of CO_2, multiply the volume from the chart by 0.812.

Illustration 6.—A square-edged orifice in a thin plate has been installed in a standard 6-in. pipe to measure the flow of a gas under the following assumed average conditions:

Volume composition of gas (dry basis). . 75 per cent H_2, 25 per cent N_2
Dew point. . . . . 80°F.
Gauge pressure . . . . 1.00 lb./sq. in.
Temperature. . . . . 85°F.
Barometer. . . . . Normal

The orifice is 3.000 in. in diameter and is installed concentrically between flanges with throat taps. The orifice differential will never be more than 1 per cent of the upstream absolute pressure.

1. Determine a value for a meter constant that when multiplied by the square root of the gauge reading in inches of mercury will give the volume in cubic feet per minute at the standard conditions of 60°F. and normal barometer. Assume that the flow is in the turbulent region at a Reynolds number of at least 30,000.

2. Calculate a correction factor by which to multiply the volume obtained from the coefficient of (1) if the actual average upstream conditions are

Volume composition of gas on dry basis.. 78 per cent H_2, 22 per cent N_2
Dew point.................... ...... 50°F.
Gauge pressure.................... 2.00 lb./sq. in.
Temperature................ .... 70°F.
Barometer...... . ... 750 mm. Hg

1. Since the differential is small, the expansion factor may be assumed to be unity. The conditions are such that ideal gases may be assumed and the orifice coefficient can be taken to be 0.610. The meter constant C_M by Eq. (VIII.72) is

$$C_M = \frac{0.610\pi(3.000)^2}{4 \times 144} \sqrt{\frac{64.4}{1 - (3.000/6.065)^4}}$$
$$= 0.248 \qquad \text{(ft., lb., sec., units)}$$

The coefficient sought is C_M''. By Eqs. (VIII.78) and (VIII.79),

$$C_M'' = C_M \frac{T_s}{p_s} \sqrt{\frac{Rp}{TM}}$$
$$R \text{ in } \frac{\text{(cu. ft.) (lb./sq. in.)}}{\text{(°R.) (lb.-moles)}} = 10.735$$

The vapor pressure of water at 80°F. $= 0.507$ lb. per sq. in.

$$\text{Mole fraction } H_2O \text{ vapor in the gas} = \frac{0.507}{15.70} = 0.0323$$
$$M_D = 0.75 \times 2.016 + 0.25 \times 28.00 = 8.510$$
$$M = 0.9677 \times 8.510 + 0.0323 \times 18 = 8.831$$
$$C_M'' = 0.248 \frac{519.6}{14.70} \sqrt{\frac{10.735 \times 15.70}{544.6 \times 8.831}} = 1.640$$

This value of C_M'' will give the volume in cubic feet per second if Δp is expressed in pounds per square foot.   To get q_s in cubic feet per minute for Δp in inches of mercury, C_M'' must be multiplied by $60 \times \sqrt{(14.70 \times 144)/29.92} = 505$.

Finally,
$$q_s = 829 \sqrt{\Delta p}$$

where q_s is in cubic feet per minute and Δp in inches of mercury.
2. The new conditions are as follows:

$$M = 7.844$$
$$p = 16.50 \text{ lb./sq. in.}$$
$$T = 529.6$$

The correction factor, by Eq. (VIII.80),

$$\sqrt{\frac{16.50}{15.70}} \sqrt{\frac{544.6}{529.6}} \sqrt{\frac{8.831}{7.844}} = 1.102$$

Note that rather slight changes in conditions above the orifice may cause a considerable error in the volume if it is not corrected.

Illustration 7.—A gas of molecular weight 58 at 90°F. and 177.5 lb. per sq. in. abs. is flowing through a 2.00-in. sharp-edged concentric orifice with a pressure drop of 50 lb. per sq. in.   The ratio of orifice diameter to pipe diameter is 0.300.   What is the rate of flow of the gas in pounds per second?

The pressure ratio is considerably less than 1.00 but greater than the critical ratio. Assuming the ideal-gas law, Eq. (VIII.62) is applicable. Correction for velocity of approach may be neglected. Assume $C_m = 0.600$.

$$\rho_m = \frac{p_m M}{RT} = \frac{(177.5 - 25)58}{10.74 \times 550} = 1.496$$

$$w \text{ (lb./sec.)} = 0.525 \times 0.600 \times 4.00 \sqrt{1.496 \times 50} = 10.9$$

Molstad and Varga[1] solved the same problem by means of their nomograph.

Illustration 8.—The flow of methane in a standard 4-in. pipe is to be measured by means of a Venturi meter with a 2.00-in.-diameter throat. If the upstream pressure is 20.0 lb. per sq. in. abs. and the temperature 90°F., what is the maximum flow in pounds per second that could be measured if the maximum possible differential is 10.00 in. Hg? Assume the Venturi coefficient is 0.980.

$$\text{Pressure ratio } r = \frac{20.00 - \dfrac{10 \times 14.7}{29.93}}{20.00}$$

$$= 0.754$$

With such a ratio the expansion factor cannot be neglected. Assuming $k = 1.30$, the expansion factor Y_1 [Eq. (VIII.56) or Fig. VIII.8] = 0.840.

$$\rho_1 = \frac{20 \times 144 \times 16.03}{1{,}544 \times 550} = 0.0543 \text{ lb./cu. ft.}$$

$$\Delta p = \frac{10 \times 14.7 \times 144}{29.93} = 709 \text{ lb./sq. ft.}$$

$$\left(\frac{D_2}{D_1}\right)^4 = \left(\frac{2.000}{4.026}\right)^4 = 0.061$$

$$A_2 = 0.0218 \text{ sq. ft.}$$

Substituting in Eq. (VIII.59),

$$w \text{ (lb./sec.)} = 0.980 \times 0.0218 \times 0.840 \sqrt{\frac{64.4 \times 709 \times 0.0543}{0.939}}$$

$$= 0.920 \text{ lb./sec.}$$

Neglect of the expansion factor would obviously cause a large error. Use of the mean density in the ordinary hydraulic equation would give $w = 1.029$, still considerably in error.

Illustration 9.—Ethylene gas, substantially pure and dry, is being metered by a sharp-edged orifice in a thin plate with throat taps. The orifice has a diameter of 1.030 in. and is installed in a 2-in. extra-heavy pipe. The average differential pressure, upstream static pressure, and temperature for a 24-hr. period, obtained from recorders, were 10.5 in. Hg, 810 lb. per sq. in. abs., and 150°F., respectively. Estimate the total number of pounds of ethylene per 24 hr.

The fractional pressure drop is so small that the expansion can be neglected, but account must be taken of the departure from the ideal-gas laws. The density of ethylene under these conditions may be obtained by any one of various methods outlined in Chap. V. We shall use the generalized compressibility-factor chart.

$$T_c \text{ (absolute critical temperature)} = 282.8°\text{K.}$$

$$p_c \text{ (absolute critical pressure)} = 50.9 \text{ atm.}$$

$$T_R = \frac{610}{1.8 \times 282.8} = 1.20, \qquad p_R = \frac{810}{14.7 \times 50.9} = 1.083$$

[1] *Loc. cit.*

Compressibility factor $= 0.77$

$$\rho = \frac{pM}{CRT} = \frac{810 \times 144 \times 28.0}{0.77 \times 1{,}544 \times 610} = 4.50 \text{ lb./cu. ft.}$$

Assume a coefficient of 0.61.

$$A_2 \text{ (orifice area)} = \frac{\pi \times (1.03)^2}{4 \times 144} \text{ sq. ft.} = 0.00580$$

$$\Delta p = \frac{10.5 \times 14.7 \times 144}{29.93} \text{ lb./sq. ft.} = 742$$

$$\left(\frac{D_2}{D_1}\right)^4 = \left(\frac{1.030}{1.930}\right)^4 = 0.0811$$

By Eq. (VIII.59),

$$w \text{ (lb./24 hr.)} = 24 \times 3{,}600 \times 0.00580 \times 0.61 \sqrt{\frac{64.4 \times 742 \times 4.50}{0.9189}}$$

$$= 148{,}000$$

Had the ideal-gas law been used, the result would have been multiplied by $\sqrt{0.77} = 0.878$, or an error of about 12 per cent. For greatest accuracy one should check the assumed value of the discharge coefficient. $Re = 2.7 \times 10^6$, and from the A.S.M.E. tables[1] C_0 is estimated to be 0.602.

Illustration 10.—Air at 70°F. and 2 ft. of water head above standard atmospheric pressure is discharging through a rounded orifice into a space maintained at 400 mm. Hg absolute pressure by means of a vacuum pump. Estimate by what per cent the volume rate of flow referred to upstream conditions will increase if the pressure in the evacuated space is dropped to 200 mm. abs.

$$p_1 = 760 + \frac{2 \times 12 \times 25.4}{13.6} = 805 \text{ mm.}$$

$$\therefore \frac{p_2}{p_1} = \frac{400}{805} = 0.497$$

This is less than the critical-pressure ratio for air (see page 332), and hence the flow is at a maximum. Any further reduction in downstream pressure will not change the flow. This principle can be utilized to maintain a constant flow of gas with a constant higher pressure and a variable lower pressure.[2]

Illustration 11.—To measure the discharge from a nitrogen compressor, the high-pressure gas (1,500 lb. per sq. in.) is to be throttled into a receiver from which the nitrogen is to discharge into the atmosphere through a flow nozzle. A pressure of 50 lb. per sq. in. gauge has been decided upon as a suitable pressure to maintain in the receiver. If the gas comes to the nozzle at this pressure and at 80°F., what throat diameter would be necessary in the nozzle if the compressor is assumed to deliver 1,200 cu. ft. per min. referred to the intake conditions of 100°F., 6 in. of water gauge pressure, and saturated with water vapor? Barometer reads 29.0 in. Hg.

This is a case where the pressure ratio p_2/p_1 is less than the critical value, and therefore Eq. (VIII.70) applies. The vapor pressure of water at 100°F. $= 0.949$ lb. per sq. in.

$$\text{Total pressure at compressor intake} = \frac{29.0 + (6/13.6)}{29.93} \times 14.70 = 14.50 \text{ lb./sq. in.}$$

[1] *Fluid Meters—Their Theory and Application*, Part 1, 4th ed., American Society of Mechanical Engineers, New York, 1937.

[2] PAGE, R. T., *Ind. Eng. Chem.*, anal. ed., **7**, 355–358 (1935).

$$\text{Mole fraction } H_2O = \frac{0.949}{14.50} = 0.0655$$

The high-pressure gas can be assumed to be dry since most of the water will have been condensed in the aftercooler.

Volume of dry nitrogen at standard conditions

$$= (1,200 \times 0.9345) \frac{14.50 \times 492}{14.70 \times 560} = 971 \text{ cu. ft./min.}$$

$$w \text{ (lb./sec.)} = \frac{971}{359 \times 60} \times 28 = 1.262$$

Assume $k = 1.41$, $C_a = 0.98$.
Substituting in Eq. (VIII.70),

$$1.262 = 0.98A_2 \times 64.3 \times 144 \sqrt{\frac{32.2 \times 1.41 \times 28}{1,544 \times 540} \left(\frac{2}{2.41}\right)^{\frac{2.41}{0.41}}}$$

$$A_2 = 0.00616 \text{ sq. ft.}$$
$$D_2 = 1.064 \text{ in.}$$

Illustration 12.—Air stored in a vessel at a pressure of 1,000 lb. per sq. in. gauge leaked at such a rate that the pressure had dropped to 900 lb. per sq. in. at the end of an hour. If the vessel were filled with hydrogen at the same temperature and pressure, what would you estimate the pressure to be at the end of an hour?

It seems reasonable to assume that Eq. (VIII.70) applies to this case, and if we assume that the temperature remains substantially constant it may be written in the special form

$$m = Kp_1 \sqrt{M} \, \theta$$

where K = constant.
    m = total weight flowing out in time θ.
    p_1 = constant pressure in the vessel.
Since the pressure is changing, the equation should be put into the differential form

$$dm = Kp \sqrt{M} \, d\theta$$

Assuming ideal gases, $$m = \frac{MpV}{RT}$$

where V is the total volume of the vessel. Since V and T remain constant,

$$dm = K'M \, dp$$

Equating, $$K'M \, dp = Kp \sqrt{M} \, d\theta$$

$$\frac{dp}{p} = \frac{K''}{\sqrt{M}} \, d\theta$$

$$\int_{1,015}^{915} \frac{dp}{p} = \frac{K''}{\sqrt{29}} \int_0^1 d\theta$$

$$K'' = -0.565$$

For the hydrogen case, $$2.303 \log \frac{p}{1,015} = \frac{-0.565}{\sqrt{2.016}}$$

$$p = 682 \text{ lb./sq. in. abs.}$$

THERMAL METERS

In principle such a meter is quite simple, but various practical difficulties have militated against the development of the principle into

useful instruments.   The addition of energy in the form of heat to a fluid stream will cause a rise in temperature, which is related to the flow by the equation

$$q = w \, \Delta H = w \int_{t_1}^{t_2} C_p \, dt \qquad \text{(VIII.88)}$$

or, for short temperature intervals,

$$w = \frac{q}{C_p(t_2 - t_1)} \qquad \text{(VIII.89)}$$

The heat energy is supplied as electrical energy in the only commercial form of this instrument (Thomas meter), and for this case Eq. (VIII.89) becomes

$$w = \frac{0.000948 E_w}{C_p(t_2 - t_1)} \qquad \text{(VIII.90)}$$

where w = flow, lb. per sec.
 E_w = electrical input, watts.
 C_p = specific heat, B.t.u. per lb. per °F.
 t = temperature, °F.

An accurate determination of w requires an exact knowledge of the specific heat of the gas in question and a measurement of the small temperature rise accurate to the order of 0.01°.   The measurement of the average temperature of a fluid stream with this degree of accuracy is an exceedingly difficult problem, but it has been accomplished in the Thomas meter by the use of resistance thermometers in the form of a wire grid that stretches across the flow channel.   In this meter the electrical input is varied to maintain a constant temperature rise because this makes the flow rate directly proportional to the electrical power supplied and greatly simplifies the problem of automatically integrating to get the total flow.   It should be borne in mind that any entrained liquid in a gas stream may cause serious errors by absorbing heat for vaporization.

FLOW OF GASES AND VAPORS THROUGH NOZZLES

Whereas the orifice and Venturi tube are used for the measurement of fluid flow, the flow nozzle is used primarily for the production of high-velocity jets that are applied to the generation of power in the turbine or to the pumping of fluids in the injector and ejector.   Details of nozzle design are beyond the scope of this book, but a few of the fundamental thermodynamic principles governing flow in nozzles will be briefly discussed.

The theoretical velocity developed by an expanding fluid, assuming the expansion to be isentropic, can be calculated from equations previously developed—Eqs. (VIII.47), (VIII.48), or (VIII.49) if the fluid is an ideal gas and Eq. (VIII.42) or (VIII.43) if the ideal-gas law is not a good assumption.   Table VIII.1 shows a series of values of velocity u_2

calculated by Eq. (VIII.48) for expansion of air from a given initial pressure of 150 lb. per sq. in. abs. and temperature of 100°F. to a series of lower pressures. Table VIII.1 also includes the molal volume of the gas at the low pressure calculated from Eq. (VII.15) and the necessary cross-sectional area of a flow nozzle to accommodate a flow of 1 lb.-mole per sec.

TABLE VIII.1—FLOW CALCULATIONS FOR A NOZZLE

p_2, lb./sq. in. abs.	u_2, ft./sec.	v_2, cu. ft./lb.-mole	A_2, sq. in.
150	negligible	40.1	
125	584	45.7	11.30
100	857	53.5	9.00
85	1,003	60.1	8.63
79.5 (critical)	1,055	63.0	8.60
75	1,098	65.7	8.62
50	1,345	87.6	9.39
25	1,639	143.5	12.61
15	1,924	206.5	15.44

Inspection of these results shows that the velocity increases and the area decreases until the critical pressure is reached $(0.53 \times p_1$ in this case); then at lower pressures the velocity continues to increase, but the area also increases. The same general result would be obtained with any gas or vapor whether ideal or not, and this leads to the conclusion that the proper shape for a nozzle to produce a high-velocity jet is a convergent passage to a throat of minimum area followed by a divergent passage, as shown diagrammatically in Fig. VIII.11. The exact shape desirable for a given set of conditions is not predictable from thermodynamics but is largely a matter of empirical determination. Given a definite shape, then one can calculate the theoretical pressure and velocity distribution along the axis from the thermodynamic equations.

FIG. VIII.11.—Diagram of a convergent-divergent nozzle.

Note that the throat area is determined entirely by the initial conditions and the flow rate desired and is independent of the low pressure.

The actual expansion of a gas in a nozzle is, of course, not strictly isentropic but is accompanied by a certain amount of friction, resulting in an increase in entropy. To compare the performance of different nozzles the engineer defines a nozzle efficiency by the equation

$$e = \frac{(u_2^2 - u_1^2)_{\text{actual}}}{(u_2^2 - u_1^2)_{\text{ideal}}} \qquad \text{(VIII.91)}$$

Thus the efficiency is defined as the ratio of the actual kinetic energy developed by the jet to the theoretical calculated from the equations, and means have been devised for measuring it experimentally. Well-designed nozzles will show efficiencies of 0.95 or even better.

The efficiency may also be expressed by

$$e = \frac{(H_1 - H_2)_{\text{actual}}}{(H_1 - H_2)_s} \tag{VIII.92}$$

as may be seen by comparing Eqs. (VIII.91) and (VIII.43). $(H_1 - H_2)_s$ is the change of enthalpy for the ideal expansion at constant S. Neglecting velocity of approach, the actual velocity can be obtained from

$$u_2 \text{ (actual)} = \sqrt{2gJ(H_1 - H_2)_s\, e} \tag{VIII.93}$$

FLOW IN PIPE LINES

Liquids.—As in the case of flow measurement the relationships are simpler for liquids owing to their incompressibility. Along with the case of liquids we can also include that of gases when the relative pressure drop is small and hence the density is substantially constant. Assuming isothermal flow (hence $E_1 = E_2$), no work mechanism in the section of pipe, and $v_1 = v_2 = v$, Eq. (VIII.4) becomes

$$z_1 - z_2 + (p_1 - p_2)v + \frac{u_1^2 - u_2^2}{2g} = -Q \tag{VIII.94}$$

Q represents the heat generated by friction in the pipe, which must all be transferred to the surroundings since isothermal conditions were assumed.

The same equation is obtained from the mechanical-energy balance as expressed by Eq. (VIII.9) except that we should have ΣF in place of $-Q$ and this has the advantage of focusing attention directly on the force of friction rather than on the ultimate result in the form of heat.

This is as far as one can get in the treatment of flow in pipe lines with the aid of thermodynamics alone. Equation (VIII.94) merely tells us how the over-all frictional loss is related to the change in static pressure in gravity head and velocity head. If the pipe is horizontal and of the same cross section at the two ends, the work done to overcome friction = $\Delta(pv)$, the decrease in static-pressure head. If the pipe is not horizontal, the pressure head may increase, decrease, or remain constant between the two sections, depending on the relative magnitudes of the friction loss and the change of potential head.

Calculation of the magnitude of the frictional loss as a function of the geometry of the pipe, the rate of flow, and the properties of the fluid would involve a consideration of the mechanism of flow, which is a

question of kinetics and outside the scope of true thermodynamics. It will be considered only very briefly here.

In the case of viscous flow in a straight cylindrical pipe of constant cross section, the work to overcome the forces of friction is readily derived from the definition of the coefficient of viscosity μ, the result being

$$F = \frac{128\mu Lq}{\pi g\rho D^4} \tag{VIII.95}$$

If the pipe is horizontal and of constant cross section, $z_2 = z_1$ and $u_2 = u_1$, and combination of Eqs. (VIII.94) and (VIII.95) gives[1]

$$\Delta p = \frac{128\mu Lq}{\pi g D^4} \tag{VIII.96}$$

one form of the well-known Poiseuille equation.

In the case of turbulent flow in a conduit without sudden changes in cross section, it is common practice to assume that the frictional loss is proportional to the square of the velocity, the length of the pipe, and wetted perimeter and inversely proportional to the cross-sectional area. This leads to one form of the well-known Fanning equation,

$$F = \frac{fLu^2 P_w}{2gA} \tag{VIII.97}$$

where P_w is the wetted perimenter or, for a circular pipe,

$$F = \frac{2fLu^2}{gD} \tag{VIII.98}$$

If the diameter and hence velocity are changing, one should consider a differential length and also eliminate u by the equation

$$u\rho = G \tag{VIII.99}$$

giving $\qquad\qquad dF = \dfrac{2fG^2\,dL}{gD\rho^2} \tag{VIII.100}$

If change in velocity head and gravity head are negligible, combination of Eqs. (VIII.94) and (VIII.98) gives

$$\Delta p = \frac{2fL\rho u^2}{gD} \tag{VIII.101}$$

$$\Delta p = \frac{2fLG^2}{g\,D\rho} \tag{VIII.102}$$

The proportionality constant, or so-called "friction factor," f can be shown by dimensional analysis to be a function of the Reynolds number. A very large amount of experimentation has been carried out in many places to establish the form of this function. It may be given either

[1] $\Delta p = p_1 - p_2$.

in graphical form or by an equation. One of the simplest equations is the following, due to Genereaux,[1] which is recommended as being on the safe side for design purposes:

$$f = 0.04Re^{-0.16} \qquad \text{(VIII.103)}$$

The equations just presented apply only to pipe lines without fittings or sudden changes in cross section. The loss in head due to flow through fittings is commonly taken care of by giving the equivalent length of straight pipe of the same diameter, which will cause the same frictional effect. The mechanical energy dissipated by friction in sudden expansions or contractions of cross section is calculated from the equations

$$F_e = \frac{u_1^2 - u_2^2}{2g} \quad \text{(expansion)} \qquad \text{(VIII.104)}$$

$$F_c = \frac{Ku_2^2}{2g} \quad \text{(contraction)} \qquad \text{(VIII.105)}$$

K is an empirical constant usually expressed as a function of the area ratio A_2/A_1. When $A_2/A_1 \rightarrow 0$, $K = 0.5$. Both these equations rest on a very slender basis of experimental fact and can be recommended only as rough approximations useful for estimating purposes.

The application of the Bernoulli theorem to flow of liquid in a pipe may now be summed up in the equation

$$z_2 - z_1 + (p_2 - p_1)v + \frac{u_2^2 - u_1^2}{2g} = F_p + F_f + F_c + F_e \quad \text{(VIII.106)}$$

1 and 2 refer to the terminal points of the whole pipe line, and F_p, F_f, F_c, and F_e are the mechanical energies converted to heat by friction in the straight pipe, fittings, sudden contractions, and sudden enlargements respectively.

Illustration 13.—A liquid whose specific gravity is 0.85 and viscosity 10 centipoises flows from a vertical cylindrical tank 6 ft. in diameter through a line of 2-in. standard pipe at the rate of 50 gal. per min. It is desired to estimate the static pressure at a point in the line that is 200 ft. of pipe from the tank and 50 ft. lower in elevation than the liquid in the tank. Fittings in the line are estimated to have an equivalent pipe length of 150 ft. The gauge pressure in the tank just above the liquid level is 20.0 lb. per sq. in.

u_1 will be assumed negligible.

$$u_2 = \frac{50 \times 144}{7.48 \times 60 \times 0.785 \times (2.07)^2} = 4.75 \text{ ft./sec.}$$

$$z_1 - z_2 = 50 \text{ ft.}$$

$$v = \frac{1}{\rho} = \frac{1}{0.85 \times 62.4} = 0.0189 \text{ cu. ft./lb.}$$

$$p_1 = 20.0 \text{ lb./sq. in. gauge}$$

[1] GENEREAUX, R. P., *Chem. Met. Eng.*, **44**, 241–248 (1937).

$$f \text{ [Eq. (VIII.103)]} = 0.04 \left(\frac{2 \times 4.75 \times 53}{12 \times 10 \times 0.000672} \right)^{-0.16} = 0.0099$$

$$F_p + F_f \text{ [Eq. (VIII.98)]} = \frac{2 \times 0.0099 \times 350 \times (4.75)^2 \times 12}{32.2 \times 2.07}$$

$$= 28.2 \text{ ft.-lb. (per lb. of fluid)}$$

$$\frac{u_1^2 - u_2^2}{2g} = -\frac{(4.75)^2}{64.4} = -0.35 \text{ ft.-lb.}$$

$$F_c = \frac{0.5 \times (4.75)^2}{64.4} = 0.18 \text{ ft.-lb.}$$

By Eq. (VIII.106), $50 + (20 - p_2) \times 144 \times 0.0189 - 0.4 = 28.2 + 0.2$

$$p_2 = 27.8 \text{ lb./sq. in. gauge}$$

Gases.—It will be assumed that the flow is isothermal (to be justified later) and that differences in elevation may be neglected. With these assumptions and the additional one that no shaft work is done in the pipe-line section under consideration, Eq. (VIII.5) reduces to

$$\frac{u_2^2 - u_1^2}{2g} = Q \tag{VIII.107}$$

This merely shows that the net energy effect in the line is an influx of heat to supply the increase in velocity head. In order to find a relation between the energy corresponding to the internal friction and the other mechanical-energy terms, we shall make use of the mechanical-energy balance given by Eq. (VIII.8), which, for this special case reduces to

$$dF + \frac{u \, du}{g} + v \, dp = 0 \tag{VIII.108}$$

Assuming that all the friction is due to turbulent flow in straight pipe or its equivalent, we may combine Eqs. (VIII.108) and (VIII.100) and obtain

$$\frac{2fG^2 \, dL}{g \, D\rho^2} + \frac{G^2 v \, dv}{g} + v \, dp = 0 \tag{VIII.109}$$

Upon dividing by v^2 (or multiplying by ρ^2), Eq. (VIII.109) becomes

$$\frac{2fG^2}{gD} \, dL + \frac{G^2}{g} \frac{dv}{v} + \rho \, dp = 0 \tag{VIII.110}$$

For an ideal gas Eq. (VIII.110) may be written

$$\frac{2fG^2}{gD} \, dL + \frac{G^2}{g} \frac{dv}{v} + \frac{M}{RT} \, p \, dp = 0. \tag{VIII.111}$$

The friction factor is a function of $Du\rho/\mu$, which is substantially a constant for a given line and mass flow rate. Integrating Eq. (VIII.111) over the whole section of length L,

$$\frac{2fG^2L}{gD} + \frac{G^2}{g} \ln \frac{v_2}{v_1} + \frac{M}{2RT} (p_2^2 - p_1^2) = 0 \tag{VIII.112}$$

or, since we have assumed ideal gases,

$$\frac{2fG^2L}{gD} + \frac{G^2}{g} \ln \frac{p_1}{p_2} + \frac{M}{2RT} (p_2^2 - p_1^2) = 0 \qquad \text{(VIII.113)}$$

This equation allows one to calculate the pressure drop $p_1 - p_2$, given the friction factor, mass rate of flow, composition of the gas (or its specific gravity), and the size of the line. The second term in Eq. (VIII.113) is negligible[1] in almost all cases, as would be expected from the fact that it represents the change in velocity head, and Eq. (VIII.113) reduces to

$$p_1^2 - p_2^2 = \frac{4fRTG^2L}{g\,DM} \qquad \text{(VIII.114)}$$

Since n, number of moles per second $= \pi GD^2/4M$, Eq. (VIII.114) can be put in the alternative form

$$p_1^2 - p_2^2 = \frac{64fRTn^2LM}{\pi^2gD^5} \qquad \text{(VIII.115)}$$

It is of interest to note that Eq. (VIII.114) is merely the so-called Fanning equation used with the arithmetic mean density. Thus,

$$\rho_m = \frac{M}{RT} \frac{p_1 + p_2}{2} \qquad \text{(VIII.116)}$$

and substitution of this in Eq. (VIII.102) gives Eq. (VIII.114).

If the flow is not isothermal, one can still use the Fanning equation with a mean density defined by the equation

$$\rho_m = \frac{M}{2R} \left(\frac{p_1}{T_1} + \frac{p_2}{T_2} \right) \qquad \text{(VIII.117)}$$

The Weymouth equation, which has been widely used for problems dealing with the flow of natural gas in long pipe lines, is simply Eq. (VIII.114) combined with the following equation for the friction factor:

$$f = 0.008D^{-\frac{1}{3}}$$

Maximum Flow.—Just as in the case of flow through nozzles, there is a maximum in the rate of flow through a pipe that can readily be found by applying the criterion

$$\frac{\partial G}{\partial p_2} \text{ at const. } p_1 \text{ and } f = 0$$

---

[1] The error in neglecting velocity head does not become appreciable until velocities of more than 100 ft. per sec. are encountered. For these special cases, Lobo, Friend, and Skaperdas [*Ind. Eng. Chem.*, **34**, 821 (1942)] developed a graphical method for solution of Eq. (VIII.113) for pressure drop which is convenient to use. In their sample problem, neglect of the velocity head causes an error of 25 per cent, but it is to be noted that the inlet velocity was 440 ft. per sec.

Performing this operation on Eq. (VIII.113), we obtain

$$G_{max} = \sqrt{\frac{gMp_2^2}{RT_2}} \qquad \text{(VIII.118)}$$

$$= \sqrt{\frac{gp_c}{v_c}} \qquad \text{(VIII.119)}$$

(Subscript c is used to denote the maximum flow case.)

Since $\qquad\qquad u = Gv$

it follows that $\qquad u_c = \sqrt{gp_cv_c} \qquad\qquad$ (VIII.120)

This is the equation for the acoustic velocity in the isothermal case, and we can conclude that a maximum velocity equal to the velocity of sound is reached in flow through a pipe.

Combining Eqs. (VIII.113) and (VIII.118) we obtain:

$$\left(\frac{p_1}{p_c}\right)^2 = 1 + \ln\left(\frac{p_1}{p_c}\right)^2 + \frac{4fL}{D} \qquad \text{(VIII.121)}$$

For a high-velocity case, f is substantially constant at 0.0040. Using this value, Eq. (VIII.121) can easily be solved by trial for p_c, the pressure at the pipe exit, which will be greater than the pressure of the space into which the pipe is discharging. With this value of p_c the maximum flow can readily be calculated from Eq. (VIII.113), which becomes

$$G_{max}^2 = \frac{(p_1^2 - p_c^2)gM}{2RT[\ln p_1/p_c + (2fL/D)]} \qquad \text{(VIII.122)}$$

As a matter of fact, the difference between Eq. (VIII.113) with p_2 equal to p_c and with p_2 equal to the pressure in the discharge space is very small in almost all cases and probably within the error involved in various assumptions and in the choice of a value for f. In other words, the question of maximum flow in a pipe is largely of academic rather than practical interest.

Isothermal vs. Adiabatic Flow.—In deriving the relationship for flow under conditions of large pressure drop, isothermal conditions were assumed. Let us now make the other limiting assumption—*viz.*, adiabatic conditions—and see what difference it would make. For these conditions and ideal gases, Eq. (VIII.4) reduces to

$$J(H_1 - H_2) = \frac{u_2^2 - u_1^2}{2g} \qquad \text{(VIII.123)}$$

or, for a narrow temperature range,

$$JC_p(T_1 - T_2) = \frac{u_2^2 - u_1^2}{2g}$$

Since $u_1/u_2 = v_1/v_2$ and $p_1v_1/T_1 = p_2v_2/T_2$, then

$$u_2 = u_1 \frac{p_1 T_2}{p_2 T_1}$$

or $$JC_p(T_1 - T_2) = \frac{u_1^2}{2g}\left[\left(\frac{p_1 T_2}{p_2 T_1}\right)^2 - 1\right] \qquad \text{(VIII.124)}$$

Assume $T_1 = 500°$R., $u_1 = 10$ ft. per sec., $p_1 = 500$ lb. per sq. in. abs., $p_2 = 100$ lb. per sq. in. abs. Solving for T_2 by trial, it is readily seen that $T_1 - T_2$ is less than 1°F. In other words, the isothermal and adiabatic assumption lead to substantially the same result. This is not unexpected because adiabatic flow in a long line is essentially nothing but a Joule-Thomson expansion or an expansion at constant H. This is readily seen from Eq. (VIII.123) to be the case as long as the velocities are not too large. For an ideal gas and approximately for any gas, an irreversible adiabatic expansion is also isothermal. If u_1 and p_1/p_2 are relatively large [Eq. (VIII.124)], then this may no longer be true.

Lapple[1] has recently considered in detail the relation between isothermal and adiabatic flow of fluids through pipe lines. An equation for adiabatic flow can be derived in the following manner starting from Eq. (VIII.108) in the form

$$\frac{u\,du}{g} + v\,dp + \frac{fu^2}{2gm}\,dL = 0 \qquad \text{(VIII.125)}$$

The relation: $pv^k = $ const. cannot be used to integrate the $v\,dp$ term, because it is true only for a reversible adiabatic expansion, but one can write

$$v\,dp = d(pv) - pv\frac{dv}{v} \qquad \text{(VIII.126)}$$

and then combining the general energy equation (VIII.6) in the particular form applying to this case (dz, dQ, and $dW_0 = 0$) with the equation

$$dE = \frac{1}{k-1}\,d(pv) \qquad \text{(VIII.127)}$$

which is merely a special form of

$$dE = C_v\,dT$$

one gets $$d(pv) = -\frac{k-1}{k}\,d\left(\frac{u^2}{2g}\right) \qquad \text{(VIII.128)}$$

Combining this with Eqs. (VIII.126) and (VIII.125) and rearranging, one obtains

$$(1+k)\frac{du}{u} - [2kgp_1v_1 + (k-1)u_1^2]\frac{du}{u^3} + \frac{kf}{m}\,dL = 0 \quad \text{(VIII.129)}$$

[1] Lapple, C. E., *Trans. Am. Inst. Chem. Engrs.*, **39**, 385–428 (1943).

This is directly integrable, and Lapple gives several integral forms. By the usual procedure for finding a maximum, it can readily be shown that again the maximum flow occurs when the velocity at the exit end of the pipe equals the velocity of sound for the case of adiabatic compression and expansion in the sound wave.

Lapple has shown that the isothermal and adiabatic flow equations give substantially the same result in the vast majority of cases, as we have shown by the simple reasoning given above. For very short pipes and relatively large pressure drop, the adiabatic discharge rate will be greater, but the maximum possible difference between the two cases is only 20 per cent.

POWER REQUIREMENT FOR PUMPING

Noncompressible Fluids.—Assuming isothermal conditions,

$$E_1 = E_2$$

and

$$p_1 v_1 - p_2 v_2 = -\frac{\Delta p}{\rho}$$

With these assumptions, Eq. (VIII.4) rearranges to

$$-W_0 = -Q + \Delta z + \frac{u_2^2 - u_1^2}{2g} + \frac{\Delta p}{\rho} \qquad \text{(VIII.130)}$$

We have already seen that $-Q = F$, the mechanical energy that is converted to heat by friction. The quantity on the right-hand side of Eq. (VIII.130) may be called the "total differential head" Δh; it is a sum of friction head, gravity head, velocity head, and static-pressure head. F will be taken to mean the work to overcome friction everywhere except in the pump itself. $-W_0$ is the theoretical work per pound of fluid. Theoretical horsepower would be given by,

$$\text{Hp.} = \frac{w \, \Delta h}{550} \qquad \text{(VIII.131)}$$

The theoretical work is that actually delivered to the fluid. The work (or power) input to the pump will be greater owing to various friction effects in the pump. This is generally taken care of by an efficiency that is known approximately for various types and sizes of pumps.

Illustration 14.—A solution of specific gravity 1.25 is to be pumped at the rate of 50 gal. per min. from an open storage tank to the top of an absorption tower. It discharges into the tower through openings equivalent in area to a 1-in. pipe. The pressure in the tower is 10 lb. gauge. The point of discharge is 80 ft. above the level of the solution in the storage tank. The pump intake is through a standard 2-in. pipe 6 ft. below the level of the solution in the tank. It discharges through a 2-in. line at substantially the same level. The friction head in the suction line is estimated

to be 2 ft. of water and in the discharge line 12 ft. of water.   If the pump has an efficiency of 70 per cent, how much power must be applied to the pump shaft?   What pressures would be indicated by gauges at the inlet and exit of the pump?

The friction head must be estimated from the given flow rate and the known geometry of the flow system by the methods already discussed.   We assume that this has been done and the above figures arrived at.

$$\text{Total friction head} = \frac{14}{1.25} = 11.2 \text{ ft. of fluid}$$

$$\text{Gravity head} = 80 \text{ ft.} \leftarrow$$

$$\text{Velocity in a 1-in. standard pipe} = \frac{50 \times 4 \times 144}{7.48 \times 60 \times \pi \times (1.315)^2} \text{ ft./sec.} = 11.8$$

$$\text{Velocity in storage tank} = 0 \text{ (assumed)}$$

$$\text{Velocity head} = \frac{(11.8)^2}{64.4} = 2.2 \text{ ft.}$$

$$\text{Pressure head} = \frac{10 \times 144}{62.4 \times 1.25} = 18.5 \text{ ft.}$$

$$\text{Total head} = 111.9 \text{ ft.}$$

$$w = \frac{50 \times 8.33}{60} \times 1.25 = 8.68 \text{ lb./sec.}$$

By Eq. (VIII.131), $\text{Theoretical hp.} = \dfrac{8.68 \times 111.9}{550} = 1.76$

$$\text{Actual hp.} = \frac{1.76}{0.70} = 2.52$$

The calculation of the pressures is readily made by applying the energy balance between two sections, one of which is located at the point where the pressure is to be determined and the other at the level of the solution in the storage tank (for intake pressure) or at the point of discharge in the tower (for exit pressure).

Thus, $$-\frac{\Delta p}{\rho} = F + \Delta z + \frac{\Delta u^2}{2g}$$

$\Delta p = p_2 - p_1$ and similarly for the other Δ's, section 2 being at the pump. For the suction line,

$$F = \frac{2}{1.25} = 1.6 \text{ ft.}$$

$$\Delta z = -6.0 \text{ ft.}$$

$$\frac{\Delta u^2}{2g} = \frac{(11.8)^2 \left(\dfrac{1.315}{2.07}\right)^4}{64.4} = 0.353 \text{ ft.}$$

$$-\frac{\Delta p}{\rho} = -4.05$$

$$\Delta p = \frac{4.05 \times 62.4 \times 1.25}{144} \text{ lb./sq. in.} = 2.19$$

The pressure at the pump inlet will be 2.19 lb. per sq. in. gauge.   Applying the same equation to the discharge line,

$$-\frac{\Delta p}{\rho} = 9.6 + 86.0 + 1.8$$

$$-\Delta p = p_1 - p_2 = \frac{97.4 \times 62.4 \times 1.25}{144} = 52.7 \text{ lb./sq. in.}$$

$$\therefore \ p_1 = 52.7 + 10.0 = 62.7 \text{ lb./sq. in. gauge}$$

Note that the theoretical pump horsepower $= w \, \Delta p/550\rho$ where Δp is the pressure differential across the pump.

$$\text{Hp.} = \frac{8.68(62.7 - 2.2)144}{550 \times 62.4 \times 1.25} = 1.76$$

This gives a check on some of the calculations.

Compressible Fluids.—If the compression is assumed to be adiabatic, which is a good assumption in practice, the theoretical power requirement for compression in a single stage is given by Eq. (VII.31), modified as follows:[1]

$$\text{Hp.} = \frac{kp_1V_1}{33,000(k-1)} \left[\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} - 1 \right] \qquad \text{(VIII.132)}$$

V_1 is the total volume taken into the compressor at p_1 in cubic feet per minute. When the pressure ratio r, is small (strictly, as $r \to 1.0$), this equation reduces to

$$\text{Hp.} = \frac{(p_2 - p_1)V}{33,000} = \frac{p_1(r-1)V}{33,000} \qquad \text{(VIII.133)}$$

which is the same as the equation for liquids. The range over which this equation is applicable can be extended greatly by using an average volume based on isothermal conditions, and this gives

$$\text{Hp.} = \frac{p_1V_1(r^2 - 1)}{33,000(2r)} \qquad \text{(VIII.134)}$$

Table VIII.2 compares these three equations for a diatomic gas at various pressure ratios, the results being expressed as a ratio of the power by Eq. (VIII.133) or (VIII.134) to that by Eq. (VIII.132).

TABLE VIII.2

r	Eq. (VIII.133)	Eq. (VIII.134)
1.01	< 1.005	< 0.995
1.05	1.02	0.995
1.10	1.035	0.990
1.25	1.088	0.977
1.50	1.16	0.969
2.00	1.31	0.977
3.00	1.56	1.038
5.00	1.95	1.170

[1] Strictly, this should be a negative power if the previous convention in regard to the sign of work is adhered to. Here and elsewhere, when there is no real need to distinguish between negative and positive quantities, the question of sign has generally been ignored.

It is evident that Eq. (VIII.133) is good only to 5 per cent up to a compression ratio of about 1.15, but Eq. (VIII.134) is good to better than 5 per cent up to a ratio as high as 3.00.

Illustration 15.—A gas mixture whose average molecular weight is 18.0 is taken from a holder at 6 in. water gauge pressure and 70°F. by a rotary gas pump and sent through a scrubbing tower to a reaction chamber in which the pressure is 1 in. Hg gauge. There is 5,000 cu. ft. per min. of the gas measured at the holder conditions. Pressure drop due to friction in all the lines and the tower is 30 in. of water. What is the theoretical horsepower of the gas booster? The pipe from the holder and into the reactor are the same size. Assume normal barometer.

Gravity head is assumed to be negligible.

$$\text{Difference in velocity heads} = 0$$

$$\text{Density of gas at holder} = \frac{14.92 \times 18 \times 144}{1,544 \times 530} = 0.0473 \text{ lb./cu. ft.}$$

$$\text{Total differential head} = \frac{30}{12} \times \frac{62.4}{0.0473} + \frac{13.6 - 6.0}{12} \times \frac{62.4}{0.0473}$$
$$= 4,135 \text{ ft.}$$

$$\text{Theoretical hp.} = \frac{5,000 \times 0.0473 \times 4,135}{550 \times 60} = 29.6$$

Illustration 16.—Natural gas, which may be assumed to be methane, is to be pumped through a 100-mile section of 40-in. inside-diameter pipe line at the rate of 150,000,000 cu. ft. per 24 hr., measured at 60°F. and standard atmospheric pressure. The gas is delivered to the pump at substantially atmospheric pressure and 60°F. and is to be at 10 lb. gauge pressure at the discharge end of the line. What power is required for pumping?

$$\text{Lb.-moles of gas per sec.} = \frac{150,000,000 \times 492}{24 \times 3,600 \times 359 \times 520} = 4.58$$

$$\text{Mass velocity } G \text{ (lb./sec./sq. ft.)} = \frac{4.58 \times 16 \times 144}{0.785 \times (40)^2} = 8.40$$

$$\frac{dG}{\mu} \text{ (Reynolds number)} = 4,090,000$$
$$f \text{ (friction factor)} = 0.0027^*$$

From Eq. (VIII.115),

$$p_1^2 - p_2^2 = \frac{64 \times 0.0027 \times 1,544 \times 520 \times (4.58)^2 \times 100 \times 5,280 \times 16}{\pi^2 \times 32.2 \times (\tfrac{40}{12})^5}$$
$$= 1.89 \times 10^8 \text{ (lb./sq. ft.)}^2$$
$$p_2^2 = [(10 + 14.7) \times 144]^2 = 1.265 \times 10^7$$
$$p_1 = 14,200 \text{ lb./sq. ft.} = 99.0 \text{ lb./sq. in. abs.}$$

By Eq. (VIII.132),

$$\text{Theoretical hp.} = \frac{1.30 \times 14.7 \times 144 \times 1.50 \times 10^8}{33,000 \times 0.30 \times 24 \times 60} \left[\left(\frac{99}{14.7} \right)^{0.231} - 1 \right] = 16,000$$

* DREW, T. B., and R. P. GENEREAUX, *Trans. Am. Inst. Chem. Eng.*, **32**, 17–19 (1936).

CHAPTER IX

HEAT TRANSFER

The great majority of operations and/or processes that are of interest to chemical engineers, whether they are physical or chemical in nature, are accompanied by a heat effect. A heat transfer must therefore occur between the system under consideration and its surroundings; in other words, either a heating or a cooling process is involved. One exception to this statement is the adiabatic process for which, by definition, there is no heat effect in the thermodynamic sense.

The transfer of heat may occur by one, or combinations, of the three fundamental mechanisms, *viz.*, (1) conduction, (2) convection, and (3) radiation.[1]

Conduction involves a transfer of energy by means of the motion and collision of the atoms and molecules of which a substance is composed. It is analogous to the process of diffusion whereby a material transfer takes place by a similar mechanism. Convection, on the other hand, transfers energy through the motion of large aggregates of molecules or by what is essentially a process of mixing. Obviously, transfer by convection can occur only in fluids, whereas conduction is the chief mechanism of transfer in solids. Conduction also occurs in fluids along with the process of convection, but the latter is so much more rapid a process that it usually entirely masks the former. Both conduction and convection require a material medium and cannot occur in a complete vacuum. This emphasizes the fundamental difference between these two processes and radiation, which proceeds best in empty space. The exact way in which energy is transferred across empty space by radiation is not understood, but for our purpose it will be convenient to regard it as occurring by means of a wave motion in a purely hypothetical nonmaterial medium (ether) about which we know practically nothing. Internal energy in a substance is assumed to be transferred in some way to wave motion in the ether; this motion is propagated in all directions, and when the waves strike a material substance the energy of the

[1] It is desirable to recall at this point that the thermodynamic definition of heat states that it is merely energy in process of transmission from one place to another by one of these mechanisms. As long as we regard the energy merely as stored or contained in a system, it cannot be regarded as heat as the term is used in thermodynamics. It is convenient, however, to have a name for the energy in a body that is capable of being transferred as heat; we shall use the term "thermal energy."

wave motion may be transmitted, reflected, or absorbed.   If absorbed, it may increase the internal energy of the body in three ways, (1) by causing a chemical reaction, (2) by increasing the kinetic energy of the molecules (temperature rise), and (3) by increasing the potential energy due to the configuration of the system (heat of vaporization, and the like).   Method 1 is rare and can be dismissed from further consideration. When the energy is absorbed by the other two means, we describe the over-all process as a "transfer of heat."

It is of interest to note that the intensity of radiation in a complete enclosure is quite independent of the nature of the material of which the enclosure is made and dependent only on the temperature.   The relation expressing this dependence is one of the most fundamental of natural laws and can be derived from thermodynamics as the following simplified treatment shows:

Assume that radiant energy in a given space can be treated thermodynamically like the energy content E of a material substance and that the total radiant energy divided by the volume gives a radiation density, or intensity, which we shall represent by ϵ.   From electromagnetic theory (and it is also easily demonstrated experimentally) radiation will exert a pressure on a solid opaque wall in its path, and this pressure is related to the energy just as the pressure of an ideal gas is related to the kinetic energy of the molecules, *viz.*,

$$p = \frac{E}{3v} \qquad \text{(IX.1)}$$

$$p = \frac{\epsilon}{3} \qquad \text{(IX.2)}$$

Let us now treat the radiation like a material and apply the well-known energy equation

$$\left(\frac{\partial E}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

Combining this with Eqs. (IX.1) and (IX.2), one gets

$$\epsilon = \frac{T}{3}\frac{d\epsilon}{dT} - \frac{\epsilon}{3}$$

or

$$\frac{d\epsilon}{\epsilon} = 4\frac{dT}{T}$$

Hence, by integration, $\ln \epsilon = \ln T^4 + \text{constant}$

or $\epsilon = bT^4 \qquad \text{(IX.3)}$

This is the Stefan-Boltzmann fourth-power law, which applies rigorously to radiation from a so-called "black body."   For present purposes the latter is merely a body that emits the maximum possible amount of

radiation for its temperature. A complete enclosure at uniform temperature is the only true black body.

For the simple case of steady-state conduction in one direction, the rate of transfer of heat is given by the equation

$$q = \frac{\Delta t}{R} \tag{IX.4}$$

or, in words,

$$\text{Quantity of heat per unit of time} = \frac{\text{temperature gradient}}{\text{resistance}}$$

Without attempting to be too precise we may say that this equation applies in a general way to practically all cases of heat transfer even though much more complex than simple linear conduction. In linear conduction Δt is merely the difference in the temperatures at two parallel planes perpendicular to the direction of transfer, and the resistance is given by

$$R = \frac{L}{kA}$$

where L is the distance between the planes, A is the area of one plane, and k is the thermal conductivity. On the other hand, in more complicated situations where the transfer occurs in more than one direction or where the path involves several materials some of which may be fluids, both Δt and R become complex functions. The further consideration of R and Δt (except as it enters into violations of the second law) is considered outside the scope of this text, and attention will be focused mainly on q, the quantity of heat involved in various changes both physical and chemical, which is just as important for any practical problem in heat transfer. In addition to the treatment of heat quantities, brief attention will be given to heating and cooling mediums and to the efficiency and operability of heat exchangers. Methods for producing temperatures below that of the surroundings is a special phase of heat transfer that will be considered in the next chapter.

HEATING AND COOLING METHODS AND MEDIUMS

Let us assume that we have a vessel containing a system to which heat is to be added or from which heat is to be removed. Since the question of whether the process is one of heating or cooling is in principle merely a question of the direction of the temperature difference, no distinction need be made and we shall generally refer to the processes as if they were heating processes, whereas in some cases actual applications may be cases of cooling. The system under consideration may be one in which a chemical reaction is occurring, or it may be a purely physical process such as vaporization. We are concerned here only

with the methods available for the transfer of the desired amount of thermal energy at a suitable rate.   We shall consider briefly, from the standpoint of general principles only, the following heating methods and mediums:

1. Hot water.
2. Steam.
3. Hot oil.
4. Organic vapors.
5. Mercury.
6. Fused salts.
7. Flue gases.
8. Electrical heating.

It is well to recall at the start that the ultimate sources of all energy for heating are (1) fuels and (2) water power (excluding minor items such as direct use of solar energy, of wind and tide power, and a few others).   The first six mediums listed are really only indirect ways of heating by means of flue gases or by radiation, which derive their energy directly from the two fundamental sources just mentioned.   Heat must first be transferred to these mediums either by conduction or convection from hot gases or by radiation from hot surfaces.   The main reason for the indirect method is that closer control of the temperature in the system being heated is thereby attained, and this is often vital to the success of the process.

One of the most important considerations in connection with any heating method, and in fact the chief one to concern us here, is the temperature level at which the energy can be made available for transfer. Obviously, it must be greater than that of the substance being heated; the difference in temperature is, for purposes of general discussion, conveniently referred to as the "thermal head" or "potential."   The available potential is directly related not only to the rate of transfer but also in many cases to the thermal efficiency.   This term refers to the fraction of the available energy in a medium that gets transferred to the desired system.   If the medium transferring heat is a gas, the potential decreases as heat is transferred and this limits the fraction of the energy that can be made available.   For example, if a process were to be carried out at 2000°F. and the heating medium were a flue gas at 2200°F., only about 10 per cent of the available energy in the gases could be utilized directly.   In a continuous process, some of the energy otherwise wasted in the exhaust gases might be transferred to materials entering the system, thus increasing the thermal efficiency.   On the other hand, if the medium is a saturated vapor, a large proportion of the energy is available at a constant potential, which is advantageous from the standpoint both of thermal efficiency and of temperature control.

Hot water has certain limited uses as a heating medium, being particularly useful in the range between 100 and 212°F. for the heating of sensitive materials that must not be heated above a given temperature limit in this range.

Saturated steam is the most desirable heating medium in the range from 212 to 600°F. It is simple to use and control, clean, and easily available and gives uniform temperature over the entire surface and high rates of heat transfer. The temperature is readily controlled at a given point by control of the pressure since it is used as a saturated vapor. In this very fact also lies the chief disadvantage of steam, *viz.*, that high temperatures can be attained only by concomitant high pressures. The following figures taken from steam tables give an idea of the temperatures possible with steam at various pressures:

Gauge pressure, lb./sq. in.	Temperature	
	°F.	°C.
250	406	208
800	518	270
1,400	587	308
2,000	636	335
3,200 (critical)	705	373

The critical temperature would be the absolute upper limit but not a practicable temperature at the present time for several reasons. Boilers for 1,400 lb. pressure are in use, but in general only much lower pressures would be available in most chemical plants, so that the practical limit for steam heating is nearer 400 to 450°F. The use of the higher pressures greatly increases the difficulties in the construction of heating surfaces, especially of the jacket type, and at high pressures the steam must be used in a coil of pipe or tubing. The Thermocoil (trade name of a commercial product) is an interesting combination of a jacket and a coil, in that the coil carrying the high-pressure steam is cast integral with the walls of the vessel to be heated.

Superheated steam can be obtained at the higher temperatures without the corresponding pressures, but it is of little use as a heating medium since one loses the two big advantages of saturated steam, *viz.*, uniformity of temperature and high transfer rate. One must also bear in mind that at temperatures of 900°F. and higher the chemical reaction between water vapor and iron surfaces becomes appreciable.

In small installations it is sometimes convenient to boost the available steam pressure by means of a reciprocating compressor. As was shown in Chap. VI the compression of saturated steam gives superheated steam,

which has just been shown to be undesirable as a heating medium.   The compression should therefore be followed by a desuperheating step. This is readily accomplished by contacting the steam with liquid water.

In the temperature range above that readily attainable with steam and up to about 1000°F., there are three methods (excluding electrical heating for the moment) that are in industrial use where uniform temperatures and close control are needed.   These are the circulation of hot oil through jackets or coils, condensation of a saturated organic vapor, and condensation of mercury vapor.   The hot-oil system uses a petroleum fraction of high flash point and is mainly useful in the range 350 to 600°F., the upper limit being set by decomposition of the oil.   The oil is circulated by a pump between the tubular heater, where it is heated by flue gases and the jacket of the vessel to which it delivers heat.   Since sensible heat rather than latent heat is being used, the temperature is not uniform over the surface, the amount of variation being a function of the heat load in relation to the rate of oil circulation.

Analogous to the use of steam is the use of the saturated vapor of an organic liquid of higher boiling point than water.   In this way one can attain temperatures higher than can be reached with steam and at much lower pressures.   There are, however, very few organic compounds that are liquid at room temperature and yet sufficiently stable at elevated temperatures for practical use.   The only compounds that have been used commercially to any extent are the aromatic compounds diphenyl and diphenyloxide.   Particularly useful is the eutectic mixture of these two known as Dowtherm A containing 73.5 per cent diphenyloxide, which has a freezing point of 53.6°F. as compared with 80.6 and 156.6°F., respectively, for diphenyloxide and diphenyl.

Dowtherm A is useful in the range from 400 to 750°F., although above 700°F. a measurable decomposition occurs and continuous operation above this temperature requires periodic purification of the material and addition of new fluid.   Its normal boiling point is 496°F., and at the two limiting temperatures given the vapor pressures are 4.1 and 150 lb. per sq. in. abs., respectively.   The vapor is produced in a boiler fired with coal, oil, or gas and is used much as steam is used.   The chief disadvantages as compared with steam are the lower temperature of decomposition, the lower rate of heat transfer, the fact that it is a combustible material and therefore offers a fire hazard, and the necessity for tighter joints in the circulating system, since leaks must be kept to a minimum to prevent loss of material.

Mercury vapor is usable in the range from 600°F. (vapor pressure about 6 lb. per sq. in. abs.) to 1000°F. (180 lb. per sq. in.), the upper limit being set by the pressure and temperature that available metals will stand.   Since mercury is an element, it is absolutely stable to tempera-

ture and the question of decomposition does not enter. It has the additional advantages of very high rate of heat transfer and no fire hazard but the disadvantages of high cost, a health hazard unless proper precautions are taken, and the necessity for extreme care in securing a leakproof system.

The use of fused salts as heat-transfer mediums is old as far as the laboratory is concerned; in relatively small baths for heat-treatment of metals they have been employed for a long time, but large-scale industrial applications are quite new. There are units now in operation with as much as 1,000,000 lb. of salt in the circulating system. The salt used in a number of installations is a mixture known as HTS, consisting of 40 per cent $NaNO_2$, 7 per cent $NaNO_3$, and 53 per cent KNO_3. It can be used over the range from 300 to 1000°F. or even to 1100°F. in some cases and is particularly useful at temperatures above the upper limit for hot oil and for Dowtherm. Its freezing point is about 290°F., low enough so that the salt can readily be melted with steam available at most plants. The salt is entirely stable up to 800°F.; above that a very slow decomposition occurs, which, however, is not serious even up to 1100°F. The coefficient of heat transfer is very good, values over 2,000 B.t.u. per hr. per sq. ft. per °F. having been reported. Another advantage of this medium is that it is used at substantially atmospheric pressure and since it has no vapor pressure the pressure does not change as the temperature level is changed. For a considerable amount of information on the properties of HTS, the reader is referred to a paper by Kirst, Nagle, and Castner.[1] It is interesting to note, in passing, that the main application of this medium at the present time is as a *cooling* agent in the Houdry process of catalytic cracking.

Since practically all energy transferred as heat is originally derived from the chemical energy of a fuel, the most direct method of heat transfer is to use the products of combustion of the fuel. The maximum temperature attainable by combustion products varies with a number of factors such as the nature of the fuel and amount of excess air used; the upper limit with air is of the order of 4000°F., and the practical limit for commonly used fuels is generally less than 3000°F. Higher temperatures may be obtained by burning the fuel with oxygen, but at the present time this is applied only on a small scale for the welding and cutting of metals. Methods for calculating the maximum flame temperature of fuels will be illustrated later in this chapter (page 415).

The chief disadvantages of heat transfer from products of combustion are poor control of temperature, fouling of heating surfaces, and the large volume of gas to be handled because of its low heat capacity. Kirst,

[1] Kirst, W. E., W. M. Nagle, and J. B. Castner, *Trans. Am. Inst. Chem. Eng.*, **36**, 371–390 (1940).

Nagle, and Castner[1] presented a calculation to compare air at 3 atm. abs. with HTS as a heat-transfer fluid.   It was assumed that each fluid was to be circulated in 1-in. pipes with a 50°F. allowable drop in temperature and the same pressure drop due to flow.   The results showed that HTS had $48\frac{1}{2}$ times the heat-carrying capacity of the air and would require only 1/1,700 as much power for circulation.   Furthermore, the heat-transfer coefficient for the salt was 30 times that of the air.

In spite of the disadvantages of direct-fired heating, it remains the only means of transferring heat at temperatures above 1100°F., with the exception of limited uses of electrical heating.

Electrical heating involves the direct conversion of electrical energy into other forms of energy that can be transferred as heat and that we have classified together under the general head of thermal energy.   From the first law, 1 kw.-hr. of electrical energy will produce 3,412 B.t.u. of thermal energy.   There are three general ways of effecting the conversion. (1) by resistance, (2) by electric arc, and (3) by induction.   The material to be heated may act as the resistance itself; the heat is thus generated directly at the point it is to be applied, and no transfer problem exists.   In other cases, special resistors, such as wires of chromium alloys or carbon or carborundum shapes, may be used, and the heat developed in the resistor is transferred to the point of application by radiation and/or convection.   The rate of heating by resistance is given by the simple relation

$$q = 3.412I^2R$$

where q = rate of heat evolution, B.t.u. per hr.
   I = mean current, amp.
   R = resistance, ohms.

A form of electric resistance heating usually called "infrared radiant heating" has become of considerable industrial importance in recent years for the drying and baking of coatings and finishes.   The heat is generated by electric currents in filaments operating at relatively low temperatures (less than 2500°K.) and by suitable reflection the infrared radiation from the filaments is directed on to the surface where the heat is to be applied.   The radiant energy striking the surface is largely absorbed (the degree of absorption depending on the nature of the surface) and converted to thermal energy.

In the induction method, the material to be heated or a container for it acts as the secondary in a step-down transformer the primary of which is a coil of wire to which an alternating current is applied; the low-voltage eddy currents generated in the material or its container are entirely converted to heat.   The frequency of the alternating current used is low

[1] *Loc. cit.*

for a magnetic material and much higher (of the order of 10,000 cycles per second) for nonmagnetic conductors. Recently, an electric heating method applicable to nonconducting materials has been developed that may solve many difficult heating problems. Unlike the previous induction methods, it does not use the transformer principle but makes the material to be heated the dielectric of a condenser in an ultra-high-frequency circuit. The molecular distortion produced by the rapid alternation of the electric field in the dielectric generates heat. Frequencies of the order of 10^6 to 10^7 cycles per second are used.

In the arc method, an electric arc is struck between two electrodes, usually carbon, after which the electrodes may be separated and the arc maintained owing to the passage of the current through vapors produced from the electrodes. The material to be heated is placed in the path of the arc or in close proximity to it.

The only limit set to the temperatures attainable by electric heating is that due to the materials used for resistors or electrodes. The highest temperature attainable in industry is that of the carbon arc (about 3600°C.); this upper limit is presumably fixed by the boiling point of carbon. Consequently, electrical heating is preeminent in the field of very high temperatures such as the manufacture of synthetic abrasives and calcium carbide. It is also used over the whole temperature range in competition with other heating methods because of certain advantages, which may be enumerated as follows:

1. Heat can be applied directly where required, often without necessity for transfer.

2. Ease of control.

3. Cleanliness.

4. Convenience in location and compactness.

5. Control of furnace atmosphere.

6. High thermal efficiency (in general, the only reason this is not 100 per cent is because of heat loss to the surroundings by radiation and convection).

HEAT EXCHANGERS

We shall deal, not with the question of heat-transfer coefficients and the capacity of exchangers, which is commonly covered in texts on heat transfer, but with a few matters of some importance not usually treated in such texts. We shall be concerned mainly with the efficiency of heat exchangers and the limiting conditions for operability.

Operability.—Let us consider the application of the two laws of thermodynamics to a simple countercurrent heat exchanger shown diagrammatically in Fig. IX.1, operating at constant pressure with any two fluids whatever. The first law demands that the following equation

hold,

$$N_A(H_{A_2} - H_{A_1}) + N_B(H_{B_1} - H_{B_2}) + Q = 0 \qquad \text{(IX.5)}$$

and the second law demands that, if A is the fluid receiving heat, the following inequality be satisfied at all sections of the exchanger,

$$t_B > t_A \qquad \text{(IX.6)}$$

Although it is obvious to anyone with only an elementary knowledge of physics that this must be true, yet it is surprising how easy it is to overlook a violation of the second law in some calculations on heat exchangers. This will be demonstrated by a few numerical illustrations.
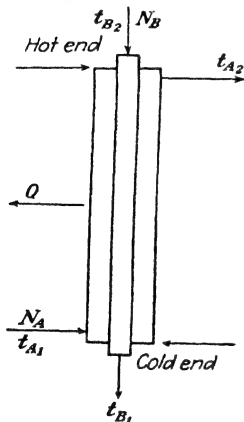
F I G . IX.1.—Diagram of countercurrent heat exchanger.

Illustration 1.—Oxygen gas at 10 atm. abs. is to enter a liquefier at 300°K. and will leave with 15 per cent liquid (quality = 0.85). It is to be cooled and partially liquefied by a countercurrent flow of oxygen at 1 atm., entering at 100°K. It is desired that the oxygen leave at 290°K. What is the mass ratio of the low-pressure to the high-pressure stream? Neglect heat exchange with the surroundings.

By Eq. (IX.5), $\qquad \dfrac{N_A}{N_B} = \dfrac{H_{B_2} - H_{B_1}}{H_{A_2} - H_{A_1}}$

The enthalpies may be evaluated from the data of Millar and Sullivan[1] as follows:

$$H_{B_2} = 3{,}232, \qquad H_{A_2} = 3{,}180$$
$$H_{B_1} = 0.85 \times 1{,}861 + 0.15 \times 550 = 1{,}666$$
$$H_{A_1} = 1{,}861$$

The units are Centigrade heat units per pound-mole.

By the equation $\qquad \dfrac{N_A}{N_B} = \dfrac{\text{moles 1 atm. gas}}{\text{moles 10 atm. gas}} = 1.19$

$$t_{B_1} = 119.7°\text{K.}$$
$$\Delta t \text{ at cold end} = 19.7°\text{C.}$$
$$\Delta t \text{ at hot end} = 10.0°\text{C.}$$

Since the terminal Δ's are positive, the exchanger appears to be operable but when the H vs. T curves for the two fluids are plotted as in Fig. IX.2 it is obvious that the calculated conditions are quite impossible since negative temperature differences occur. Since the values of ΔH for the two fluids from either terminus to any level must be equal in the case of any adiabatic exchanger, the temperature difference at any section in the exchanger is given by the horizontal distance between the two curves.

It is particularly easy to fall into a second-law violation with an exchanger in which a phase change occurs. However, it can also happen when there is no phase change, as Illustration 2 shows.

[1] MILLAR, R. W., and J. D. SULLIVAN. Thermodynamic Properties of Oxygen and Nitrogen, *U. S. Bur. Mines Tech. Paper* **424** (1928).

Illustration 2.—Air at 75 atm. and 300°K. is to be cooled in a countercurrent exchanger to 100°K. by nitrogen entering at 1 atm. and 80°K. There are 1.75 moles of nitrogen per mole of air. At what temperature should the nitrogen leave, neglecting heat leakage into the exchanger?

The enthalpies of the air [on the same basis as the N_2 data in the paper of Millar and Sullivan (*op. cit.*)] and nitrogen, in centigrade heat units per pound-mole, are

$$H_{B_2} = 2,854, \qquad H_{B_1} = 280, \qquad H_{A_1} = 1,352$$

From an energy balance,
$$H_{A_2} = 2,822$$
$$t_{A_2} = 291°K.$$
$$\Delta t_2 = 9°C., \qquad \Delta t_1 = 20°C.$$

A plot of the H vs. T curves in Fig. IX.3 shows that the proposed conditions are impossible. The dotted line tangent to the HT curve of the air corresponds to the
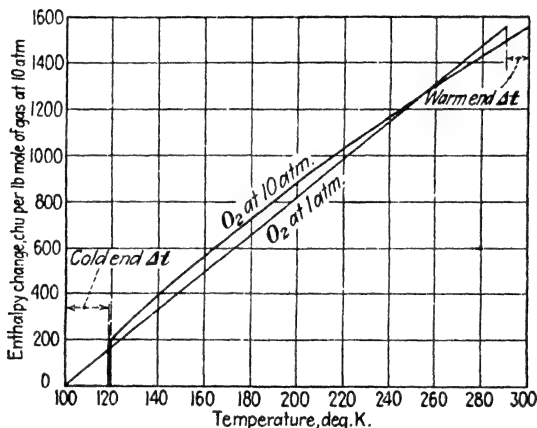
Fig. IX.2.—Violation of the second law of thermodynamics in a heat exchanger (case of a phase change in one of the fluids).

minimum possible amount of N_2 that could be used, *viz.*, 2.10 moles per mole of air, and shows that it cannot leave at a temperature above 255°K. This assumes that the heat capacity of the nitrogen is a constant, which is a close approximation.

For an adiabatic exchanger in which no phase change occurs, Eq. (IX.5) can be written

$$w_A \bar{c}_{p_A}(t_{A_2} - t_{A_1}) = w_B \bar{c}_{p_B}(t_{B_2} - t_{B_1}) \qquad (IX.7)$$

where w_A and w_B = mass flow rates.

$\bar{c}_{p_A}$ and $\bar{c}_{p_B}$ = mean specific heats.

Or
$$k(t_{A_2} - t_{A_1}) = (t_{B_2} - t_{B_1}) \qquad (IX.8)$$
where
$$k = w_A \bar{c}_{p_A}/w_B \bar{c}_{p_B}.$$
When $k > 1$,
$$t_{B_2} - t_{A_2} > t_{B_1} - t_{A_1}$$
or
$$\Delta t_2 > \Delta t_1 \qquad (IX.9)$$
Similarly, when $k < 1$;
$$\Delta t_2 < \Delta t_1 \qquad (IX.10)$$

If $\Delta t_2 > \Delta t_1$, it is clear that only the cold end Δt can be made to approach zero and there must inherently be a finite Δt at the hot end no matter how large the exchanger is. If $\Delta t_2 < \Delta t_1$, the converse is true. Otherwise the Ht curves would cross and the second law be violated. We may state these facts in the following simple but useful rule:

When the fluid receiving heat has the greater heat capacity, only the cold end Δt can be made to approach zero. When it has the smaller heat capacity, only the hot end Δt can be made to approach zero.
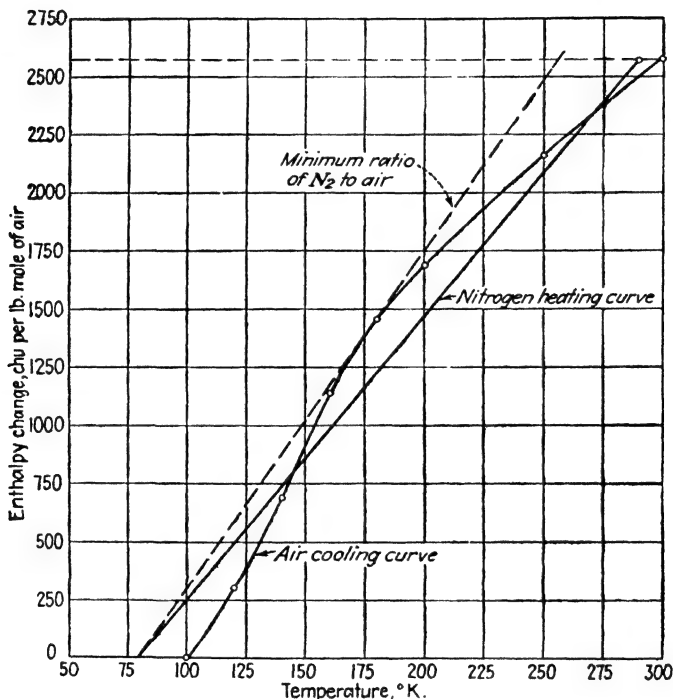
Fig. IX.3.—Violation of the second law of thermodynamics in a heat exchanger (case in which no phase change occurs in either fluid).

If the exchanger is not adiabatic, the situation is not so simple. For example, by the same reasoning used above, it can be shown that, when the exchanger loses heat to the surroundings, the hot-end Δt must be greater than the cold-end Δt when the fluid receiving heat has the greater heat capacity, or, in other words, the rule stated above still applies. But when there is a heat leak in, Δt at the hot end may be greater than, equal to, or less than the Δt at the cold end, depending on the magnitude of the heat transfer from the surroundings.

Efficiency of a Heat Exchanger.—This is generally defined on the basis of the temperature approach at one of the ends of the exchanger. The closer the approach, the more efficient is the exchanger; one that brings the two temperatures only $dt°$ apart would have 100 per cent efficiency. However, we have just seen that there are certain limitations set by the second law on the possible temperature approaches. For example, it is evident from the preceding discussion that under certain circumstances it would not be possible to obtain a close approach at either end; under other conditions, one might obtain a close approach at either the hot end or the cold end but not at both. If, however, we restrict our discussion to the case where the Ht lines of the two fluids are substantially linear, then we have two simple cases:

Case (a).—Heat capacity of the fluid receiving heat (fluid A) is less than that of the fluid delivering heat. In this case, the hot-end Δt can approach zero, and

$$e = \text{efficiency} = \frac{\text{actual temperature rise of fluid } A}{\text{maximum possible rise of temperature}} = \frac{t_{A_2} - t_{A_1}}{t_{B_2} - t_{A_1}}$$

(IX.11)

Some prefer to express results in terms of the "inefficiency," which for this case is given by

$$1 - e = \frac{\Delta t_2}{t_{B_2} - t_{A_1}} \tag{IX.12}$$

Case (b).—Heat capacity of the fluid receiving heat is greater than that of the fluid delivering heat.

The cold-end Δt is now the one that can be made to approach zero, and we have

$$e = \frac{t_{B_2} - t_{B_1}}{t_{B_2} - t_{A_1}} \tag{IX.13}$$

$$1 - e = \frac{\Delta t_1}{t_{B_2} - t_{A_1}} \tag{IX.14}$$

Illustration 3.—Assume that 100 lb. per hr. of fluid B leave a still at 400°F. It is desired to design an exchanger that will transfer the heat in this fluid to another fluid A that is at 80°F. and that will flow at the rate of 90 lb. per hr. Fluid B has a specific heat of 0.55 B.t.u. per lb. per °F., and A a specific heat of 0.48 B.t.u. per lb. The exchanger is to have an efficiency of 98 per cent. Neglecting heat loss, what should the terminal Δt's be?

By Eq. (IX.12) $\Delta t_2 = 0.02(400 - 80) = 6.4°F.$

Then $t_{A_2} = 393.6$

$$k = \frac{90 \times 0.48}{100 \times 0.55} = 0.785$$

By Eq. (IX.8), $t_{B_1} = 400 - 0.785(393.6 - 80)$

$$= 154°F.$$

$$\Delta t_1 = 74°F.$$

HEAT EFFECTS OF PHYSICAL PROCESSES

Let us make a general subdivision of all heat effects that accompany processes into two categories, *viz.*, those accompanying (1) physical processes and (2) chemical processes. In this section we shall consider only physical processes where the heat effects may be further classified as

1. Sensible-heat changes (*i.e.*, heat effects accompanied by temperature change).
   a. Pure gases.
   b. Pure liquids.
   c. Pure solids.
   d. Solutions.
2. Heat of phase change (constant temperature in case of single component).
   a. Solid-solid.
   b. Solid-liquid.
   c. Solid-vapor.
   d. Liquid-vapor.

Sensible-heat Changes of Fluids.—In this section we shall be concerned only with the effect of temperature on the specific heat and enthalpy of pure fluids (*i.e.*, single component). The effect of pressure has already been treated in Chap. VI. Strictly speaking, we are to deal with $C_p\circ$ and $H°$, the values at zero pressure, but practically we need make no distinction between the values at $p = 0$ and those at atmospheric pressure. The values at zero pressure can be calculated from spectroscopic measurements, and these are probably more accurate than those obtained from thermal measurements when the band spectra are well known and the molecule is relatively simple. The methods of making such calculations are beyond the province of this book; for information on this subject the student is referred to the book by Wenner.[1]

For a monatomic gas, the kinetic theory of gases predicts that C_p (molal) is independent of temperature and equal to $\frac{5}{2}R$, or 4.96, g.-cal. per g.-mole per °C., and this has been amply confirmed by experiment. In the case of all gases of greater molecular complexity, the specific heat increases with the temperature. Three equations in particular have been used to represent empirically the instantaneous C_p as a function of temperature, *viz.*,

$$C_p = \alpha + \beta t + \gamma t^2 + \cdots \tag{IX.15}$$
$$C_p = a + bt + ct^{-2} \tag{IX.16}$$
$$C_p = A + Bt + Ct^{-\frac{1}{2}} \tag{IX.17}$$

The temperature may be either on the centigrade or Fahrenheit scale or on an absolute scale. The corresponding equations for H are readily obtained by integration, that corresponding to Eq. (IX.15) being

$$H = H_0 + \alpha t + \tfrac{1}{2}\beta t^2 + \tfrac{1}{3}\gamma t^3 + \cdots \tag{IX.18}$$

[1] WENNER, R. R., "Thermochemical Calculations," McGraw-Hill Book Company, Inc., New York, 1941.

where H_0 is a constant of integration whose value is determined by fixing H arbitrarily at some temperature. The usual proceeding is to make $H = 0$ at $t = 0°C$. The following equations for mean C_p between the range t_1 to t_2 are also readily obtained from the instantaneous C_p equations, using the definition given by Eq. (I.32):

$$\bar{C}_p = \alpha + \tfrac{1}{2}\beta(t_1 + t_2) + \tfrac{1}{3}\gamma(t_1^2 + t_1 t_2 + t_2^2) + \cdots \tag{IX.19}$$

$$\bar{C}_p = a + \frac{1}{2}b(t_1 + t_2) + \frac{c}{t_1 t_2} \tag{IX.20}$$

$$\bar{C}_p = A + \frac{1}{2}B(t_1 + t_2) + \frac{2C}{\sqrt{t_2} + \sqrt{t_1}} \tag{IX.21}$$

The question as to which of these empirical specific-heat equations is the best cannot be given a general answer. For example, Thompson[1] compared them for the gases CO_2, CO, H_2O, H_2, and O_2 and found that Eq. (IX.15) was best for CO and H_2O, Eq. (IX.16) was best for H_2, and Eq. (IX.17) was best for CO_2 and O_2.

It is convenient to take the base temperature for mean C_p at $t = 0°C.$, and then Eq. (IX.19) reduces to

$$\bar{C}_p = \alpha + \tfrac{1}{2}\beta t + \tfrac{1}{3}\gamma t^2 + \cdots \tag{IX.22}$$

TABLE IX.1.—CONSTANTS OF THE ENTHALPY-TEMPERATURE EQUATION BASED ON THE
SPECIFIC-HEAT EQUATIONS OF BRYANT
Units: C_p in c.h.u. per lb.-mole per °K.
T in °K. over the range $300 - 2000°K$.
$H = 0$ at $T = 273.2°K$.

Gas	α	$\beta \times 10^3$	$\gamma \times 10^7$	H_0
O_2	6.26	2.746	$- 7.70$	$-1,808$
N_2	6.30	1.819	$- 3.45$	$-1,787$
H_2	6.88	0.066	2.79	$-1,880$
CO_2	6.85	8.533	-24.75	$-2,173$
CO	6.25	2.091	$- 4.59$	$-1,782$
H_2O	6.89	3.283	3.43	$-2,007$
NO	6.21	2.436	$- 6.12$	$-1,784$
HCl	6.64	0.959	$- 0.57$	$-1,850$
HBr	6.30	1.819	$- 3.45$	$-1,787$
CH_4	3.38	17.905	-41.88	$-1,563$
HI	6.25	2.091	$- 4.59$	$-1,782$
H_2S	6.48	5.558	-12.04	$-1,970$
SO_2	8.12	6.825	-21.03	$-2,459$
HCN	7.01	6.6	-16.42	$-2,150$
COS	8.32	7.224	-21.46	$-2,528$
CS_2	9.76	6.102	-18.94	$-2,881$
NH_3	5.92	8.963	-17.64	$-1,940$
C_2H_2	8.28	10.50	-26.44	$-2,636$

[1] THOMPSON, M. DE K., *Electrochem. Soc. Preprint* 82-8, Oct. 12, 1942.

TABLE IX.2.—MEAN SPECIFIC HEAT OF GASES BETWEEN 0 AND $t°C$. AND AT
ZERO PRESSURE
Units: g.-cal./g.-mole

$t°C$.	H_2	N_2	O_2	CO	NO	H_2O	CO_2	N_2O	SO_2	Air
100	6.92	6.97	7.05	6.97	7.14	8.03	9.17	9.79	9.74	6.96
200	6.95	7.00	7.15	7.00	7.17	8.12	9 65	10.12	10.15	7.01
300	6.97	7.04	7.26	7.06	7.22	8.22	10.06	10.45	10.52	7.06
400	6.98	7.09	7.38	7.12	7.30	8.34	10.40	10.74	10.84	7.13
500	6.99	7.15	7.49	7.19	7.38	8.47	10.75	11.02	11.11	7.20
600	7.01	7.21	7.59	7.27	7.46	8.60	11.03	11.24	11.35	7.27
700	7.03	7.27	7.68	7.34	7.54	8.74	11.28	11.50	11.55	7.34
800	7.06	7.35	7.77	7.43	7.62	8.89	11 50	11.71	11.72	7.42
900	7.09	7.42	7.85	7.50	7.70	9.04	11.70	11.90	11.88	7.49
1000	7.12	7.49	7.92	7.57	7.76	9.18	11.88	12.07	12.01	7.56
1100	7.15	7.56	7.98	7.64	7.83	9.32	12.05	12.21	12.13	7.62
1200	7.20	7.62	8.04	7.70	7.89	9.45	12.19	12.35	12.23	7.68
1300	7.24	7.67	8.11	7.76	7.94	9.58	12.32	12.48	12.33	7.73
1400	7.28	7.73	8.16	7.81	7.99	9.72	12.45	12.60	12.41	7.78
1500	7.32	7 78	8.20	7.85	8.03	9.84	12.56	12.69	12.48	7.84
1600	7.36	7.82	8.24	7.90	8.08	9.96	12.66	12.78	12.55	7.88
1700	7.40	7.86	8.28	7.94	8.12	10.09	12.75	12.88	12.61	7.92
1800	7.45	7.91	8.33	7.98	8.15	10.20	12.84	12.95	12.67	7.96
1900	7.49	7.94	8.38	8.02	8.19	10.30	12.92	13.01	12.71	7.99
2000	7.53	7.98	8.42	8.05	8.22	10.41	12.99	13.09	12.77	8.03
2100	7.57	8.01	8.45	8.09	8.26	10.52	13.06	13.17	12.81	8.06
2200	7.62	8.05	8.48	8.12	8.29	10.61	13.13	13.21	12.85	8.08
2300	7.66	8.08	8.52	8.15	8.31	10.71	13.19	13.28	12.89	8.12
2400	7.70	8.10	8.56	8.18	8.34	10.79	13.24	13.33	12.93	8.14
2500	7.74	8.14	8.59	8.21	8.36	10.87	13.30	13.38	12.96	8.18
2600	7.78	8.17	8.63	8.24	8.38	10.96	13.34	13.42	12.99	8.20
2700	7.81	8.19	8.65	8.26	8.40	11.03	13.39	13.46	13.02	8.23
2800	7.85	8.22	8.68	8.28	8.42	11.11	13.43	13.51	13.04	8.25
2900	7.89	8.24	8.72	8.30	8.44	11.18	13.48	13.55	13.07	8.27
3000	7.92	8.26	8.76	8.32	8 45	11.23	13.52	13.59	13.10	8.29

and ΔH between any two temperatures is given by

$$\Delta H = \bar{C}_{p_1}t_2 - \bar{C}_{p_1}t_1 \qquad (IX.23)$$

Values of ΔH are very easily obtained from a graph of Eq. (IX.18), which
is commonly called a "sensible-heat diagram." For more accurate
values than could be read from the usual small-scale chart a tabulation
of either H or $\bar{C}_p$ is more convenient than a larger diagram.

Constants of Eq. (IX.15) for a number of common gases are given by Eastman,[1] Spencer and Justice,[2] and Bryant.[3] The constants of Eq. (IX.18) from the C_p equations of Bryant are given in Table IX.1.

Heck[4] has tabulated instantaneous C_p and H for N_2, O_2, CO, H_2, CO_2, and H_2O over the range from 600 to 5400°R., the values being based on spectroscopic data. A tabulation of mean C_p is particularly advantageous for calculation of heat effects; such a table for a number of gases was given by Justi and Lüder[5] and is reproduced in part in Table IX.2.[6] It is easy to obtain accurate values of the heat effect for heating or cooling a gas from this table.

Illustration 4.—How much heat must be added to change the temperature of 100 lb. of air from 500 to 2250°C.?

From Table IX.2, $t_1 = 500$, $\bar{C}_{p_1} = 7.20$ $t_2 = 2,250$, $\bar{C}_{p_2} = 8.10$

By Eq. (IX.23),

$$Q = N\,\Delta H = \tfrac{100}{29}\,(8.10 \times 2,250 - 7.20 \times 500) = 50,300 \text{ c.h.u.}$$

Values of the first three constants in Eq. (IX.18) for various hydrocarbons, based on the data of Edmister,[7] are given in Table IX.3.

TABLE IX.3.—CONSTANTS OF ENTHALPY-TEMPERATURE EQUATION FOR VARIOUS HYDROCARBONS*

Gas	α	β	H_0
CH_4	4.60	0.0133	$-1,753$
C_2H_2	7.51	0.01115	$-2,466$
C_2H_4	3.84	0.022	$-1,870$
C_2H_6	3.84	0.0298	$-2,161$
C_3H_6	4.09	0.0372	$-2,506$
C_3H_8	4.09	0.0432	$-2,730$
C_4H_8	4.60	0.0515	$-3,179$
C_4H_{10}	4.60	0.0562	$-3,354$
C_5H_{12}	5.11	0.0692	$-3,979$
C_6H_{14}	5.62	0.0822	$-4,603$
C_7H_{16}	6.13	0.0952	$-5,228$
C_6H_6	6.61	0.0526	$-3,646$

* Units are C_p in c.h.u. per lb.-mole per °K. and temperature in °K. Temperature range, 250 to 600°K.

Edmister found that C_p for paraffin and olefin hydrocarbons containing three or more carbon atoms could be related to the numbers of carbon and

[1] EASTMAN, E. D., *U.S. Bur. Mines Tech. Paper* 445 (1929).
[2] SPENCER, H. M., and J. L. JUSTICE, *J. Am. Chem. Soc.*, **56**, 2311–2312 (1934).
[3] BRYANT, W. M. D., *Ind. Eng. Chem.*, **25**, 820–823 (1933).
[4] HECK, R. C. H., *Mech. Eng.*, January, 1940, pp. 9–12.
[5] JUSTI, E., and H. LÜDER, *Forsch. Gebiete Ingenieurw.*, **6**, 211 (1935).
[6] Justi and Lüder's values for D_2, HD, OH, and D_2O have been omitted.
[7] EDMISTER, W. C., *Ind. Eng. Chem.*, **30**, 352 (1938).

hydrogen atoms by the equation

$$C_p \text{ (c.h.u./lb.-mole/}°\text{K.)} = 2.56 + 0.51n + (0.0013n^2 + 0.0044n$$
$$- 0.00065mn + 0.00495m - 0.0057)T \quad (\text{IX.24})$$

where n = number of carbon atoms.

   m = number of hydrogen atoms.

   T = degrees Kelvin.

Spencer and Flannagan[1] present the constants of Eq. (IX.15) or (IX.16) for 61 tri- and polyatomic gases based on calculations from spectroscopic data.

It is important again to emphasize the empirical nature of the C_p and H equations that have been presented and to stress the fact that they should not be used for extrapolation. For example, they are quite erroneous for temperatures below 0°C., and in some cases equations of the form of Eq. (IX.15) may pass through a maximum, a behavior that is quite contrary to fact. It is also well to bear in mind that much of the available specific heat data is not of great accuracy. Equations that are supposed to represent C_p for the same gas may differ as much as 10 per cent or more in some cases.

Relation of C_p to Structure of Organic Molecules.—In heating and cooling problems one may have to deal with any one of a large number of organic compounds and to simplify the problem of obtaining the thermodynamic properties, it is desirable to relate the property to structure. Bennewitz and Rossner[2] presented a method of calculating C_p for organic molecules whose structure involved seven different bonds between C, H. and O. Fugassi and Rudy[3] simplified the use of the method, and Dobratz[4] introduced a modification to improve the accuracy and also added data for bonds involving N, S, and the halogens. The equation of Dobratz is

$$C_v \text{ (at } p = 0) = 3R + \frac{aR}{2} + \Sigma q_i C \nu_i + \frac{3n - 6 - a - \Sigma q_i}{\Sigma q_i} \Sigma q_i C \delta_i \quad (\text{IX.25})$$

where a = number of bonds permitting free rotation (C—C or C—O in ethers and esters).

   Σq_i = number of valence bonds of all types.

   $C_{\nu i}$ and $C_{\delta i}$ are Einstein functions.[5]

   n = number of atoms in the molecule.

[1] SPENCER, H. M., and G. N. FLANNAGAN, *J. Am. Chem. Soc.*, **64**, 250–253 (1942).

[2] BENNEWITZ, K., and W. ROSSNER, *Z. physik. Chem.*, **39B**, 126 (1938).

[3] FUGASSI, P., and C. L. RUDY, JR., *Ind. Eng. Chem.*, **30**, 1029–1030 (1938).

[4] DOBRATZ, C. J., *Ind. Eng. Chem.*, **33**, 759–762 (1941).

[5] A derivative of energy with respect to temperature, in other words, a specific heat at constant volume.

$\Sigma q_i C_{v i}$ (or $\Sigma q_i C_{\delta i}$) is the summation of the products of the number of bonds of a given type and the corresponding value of the Einstein function for that bond. C_v = specific heat at constant volume, in gram-calories per gram-mole per degree centigrade. The Einstein functions are evaluated from bonding frequencies, and for convenience of use they are represented as functions of temperature by equations of the form

$$C_v \text{ (or } C_\delta) = A + BT + CT^2 \tag{IX.26}$$

Values of the constants of this equation for each bond are tabulated in Dobratz's paper. From the value of C_v obtained by this method, C_p can be calculated by methods previously illustrated (see Chap. VI). Considering the various uncertainties involved it is probable that one is not justified in using anything more complex than $C_p - C_v = R$.

The method is quite simple to use. For example, consider the case of acetone vapor. In this molecule there are six C—H bonds, two C—C bonds, and one C==O so that $\Sigma q_i = 9$, $a = 2$, and $n = 10$. The constants of Eq. (IX.26) for the two frequencies (ν and δ) are obtained from the table for each bond and multiplied by the number of bonds of that type. Substituting in Eq. (IX.25) gives an equation for C_v of the same form as Eq. (IX.26). The articles referred to may be consulted for further details.

Liquids.—The variation of the specific heat of liquids with the temperature is less important than that of gases since the former are heated or cooled over much shorter ranges. In general, it may be stated that C_p increases with the temperature, and Eq. (IX.15) is commonly used to represent the relation, though more than two constants are seldom justified. The great majority of liquids will have values of C_p per pound lying between the limits 0.40 and 0.50. Some exceptions are the higher values for water, ammonia, and methane and the lower values for mercury and chlorinated compounds.

Heat Capacity of Solids.—Classical theory predicted the maximum value of atomic C_v to be $3R$, or 5.96, which corresponds to a C_p of about 6.2, the value for elements at room temperature according to the old rule of Dulong and Petit. This rule holds pretty well except for elements of atomic weight less than 40. For these light elements the value of C_p is less than the value called for by the rule as indicated below. For compounds one can use Kopp's rule for a first approximation, *viz.*, that C_p of a compound = ΣC_p of the atoms or 6.2 times the number of atoms, in the majority of cases. For certain light elements, however, the following values are suggested in place of 6.2: C, 1.8; H, 2.3; B, 2.7; Si, 3.8; O, 4.0; F, 5.0; P, 5.4; S, 5.4. The specific heat of solids is less than that of liquids and also increases with the temperature. The relationship has

generally been represented by Eq. (IX.15), but Kelley[1] has found Eq. (IX.16) to be a preferable form.

The specific heat of solids at low temperatures is not of great practical importance in a direct sense, but it is of considerable scientific interest and is of importance in the understanding of the third law of thermodynamics and in the evaluation of absolute entropy. For this reason it is desirable to treat it briefly.

A number of investigators have attacked the general problem of relating the specific heat to temperature with the aid of the quantum theory. In particular, Einstein and Debye have derived relationships between C_v and T involving vibration frequencies of the atoms and molecules. These relations are not suitable for practical application, but certain simplified relationships that come from them may be useful to the engineer. For example, the relation for a monatomic solid can be put in the form

$$C_v = \phi\left(\frac{T}{\theta}\right) \tag{IX.27}$$

where ϕ is the same function for all solids of this class and θ is a temperature characteristic of each substance. In other words, a single determination of C_v serves to fix the value of θ and hence the whole C_v vs. T curve once this curve has been established for some one substance of this class. This one value of C_v should be determined at some temperature well below that where $C_v = 3R$. In practice, it has been found most convenient to plot C_v against $\log (T/\theta)$.

Lewis and Gibson[2] extended this relationship to elements of more complex structure and even to compounds by putting it in the form

$$C_v = \phi\left(\frac{T}{\theta}\right)^n \tag{IX.28}$$

where the function is the same as that of Eq. (IX.27) and n is an additional characteristic constant that is always less than 1.0. Writing the equation in the form

$$C_v = \phi\left(n \log \frac{T}{\theta}\right) \tag{IX.29}$$

it can readily be shown that

$$n = \frac{\alpha_1 - \alpha_2}{\log T_1 - \log T_2} \tag{IX.30}$$

and

$$\log \theta = \log T_1 - \frac{\alpha_1}{n}$$

where α_1 and α_2 are two values of $n \log (T/\theta)$ corresponding to two measured values of C_v, which can be read from a graph applying to the previous class since the functions are the same.

[1] KELLEY, K. K., U.S. Bur. Mines Bull. 371 (1934).
[2] LEWIS, G. N., and R. E. GIBSON, J. Am. Chem. Soc., 39, 2554 (1917).

At very low temperatures approaching absolute zero, the Debye equation for C_v as a function of temperature reduces to

$$C_v = aT^3 \qquad (IX.31)$$

which shows that $C_v = 0$ at $T = 0$ since a is a constant. From Eq. (IX.31) one can readily derive

$$S = \tfrac{1}{3}aT^3 \qquad (IX.32)$$

and hence $S = 0$ at $T = 0$. When properly restricted the latter equation is a statement of the third law; hence, we see that this law is closely bound up with the specific heats of solids in the neighborhood of $T = 0$.

For a comprehensive review of the data on the specific heats of inorganic compounds, both above and below room temperature, the student is referred to two U.S. Bureau of Mines bulletins by Kelley.[1]

Heat of Phase Change (Single Component).—The Clausius-Clapeyron equation is the fundamental equation relating a latent heat for any type of phase change to other quantities, but to calculate this heat one requires accurate data relating the equilibrium pressure to the temperature and data on the volumes of the two phases. If these data were always available, our discussion need go no further; but the fact is that they are seldom available and we need some empirical relationships for calculating latent heats with sufficient accuracy for engineering purposes. In this section we shall be concerned with such relationships primarily for heat of vaporization.

Latent Heat at the Normal Boiling Point.—One of the oldest and simplest relations for this is Trouton's rule, which may be stated as follows:

$$\frac{L}{T} \text{ (molal entropy of vaporization)} = \text{a constant}$$

It is restricted to the normal boiling point. The "constant" actually varies considerably but averages about 21 for a number of substances. A few typical values chosen particularly to show the departures from the rule are as follows:

Hydrogen	10.6
Nitrogen	17.3
Ammonia	23.2
Aniline	21.1
Ethyl acetate	22.0
Ethyl alcohol	26.8
Water	26.0
Octane	20.4

[1] KELLEY, K. K., High Temperature Specific Heat Equations for Inorganic Substances, *U.S. Bur. Mines Bull.* 371 (1934); The Entropies of Inorganic Substances, *U.S. Bur. Mines Bull.* 350 (1932).

A more complex relation also applying at the normal boiling point is the following one:

$$L/T = \frac{R \ln p_c[1 - (1/p_c)]}{1 - (T_B/T_c)} \tag{IX.33}$$

which works fairly well for a variety of substances but requires a knowledge of the critical state.

Kistiakowsky[1] found the very simple equation

$$L = v \ln v \tag{IX.34}$$

to hold remarkably well at the normal boiling point, where L is in cubic centimeter-atmospheres when $v = $ molal volume in cubic centimeters. Applying the ideal-gas law to the vapor converts this equation to the more usual form

$$\frac{L}{T} = 8.75 + 4.571 \log T \tag{IX.35}$$

where L is in gram-calories per gram-mole and T in degrees Kelvin. He found agreement within 3 per cent for 60 nonpolar substances.

Latent Heat as a Function of Temperature.—Hildebrand[2] noticed that the entropy of vaporization was a function of molal vapor concentration. Lewis and Weber[3] and McAdams and Morrell[4] developed this idea by plotting L/T vs. $\log p/T$ (since p/T is proportional to vapor concentration for ideal gases). Two lines can be drawn that are roughly linear, one for nonpolar liquids and one for polar liquids like water and alcohols. The relationship represented by these lines, generally known as the "Hildebrand function," can be used over a range of temperatures but breaks down as one approaches the critical region.

Watson[5] plotted $(L/T)f$ vs. T_R, where f is a constant characteristic of each substance, and found the data for all liquids, both polar and nonpolar, to fall on one curve. The plot can be used to obtain relative values of L/T or the same relation can be put in the following algebraic form:[6]

$$\frac{L}{L_1} = \left(\frac{1 - T_R}{1 - T_{R_1}}\right)^{0.38} \tag{IX.36}$$

The value of L_1 can be obtained by one of the methods given above for the normal boiling point. This method requires only a knowledge of the critical temperature to give the complete range of latent heats.

[1] KISTIAKOWSKY, W., *Z. physik. Chem.*, **107**, 65–73 (1923).
[2] HILDEBRAND, J. H., *J. Am. Chem. Soc.*, **37**, 970 (1915).
[3] LEWIS, W. K., and H. WEBER, *Ind. Eng. Chem.*, **14**, 485 (1922).
[4] McADAMS, W. H., and J. MORRELL, *Ind. Eng. Chem.*, **16**, 375 (1924).
[5] WATSON, K., *Ind. Eng. Chem.*, **23**, 362 (1931).
[6] WATSON, K., *Ind. Eng. Chem.*, **35**, 398 (1943).

From the Clausius-Clapeyron equation and the vapor-pressure equation (VI.59), Watson derived the following equation for latent heat at the normal boiling point,

$$L_B = 0.95RB \left(\frac{T_B}{T_B - 43} \right)^2 \qquad \text{(IX.37)}$$

which is then combined with Eq. (IX.36) to give an equation for calculating L at any temperature from p_c, T_c, and T_B. [B is a constant of Eq. (VI.59) that can be evaluated from these three quantities.]

Othmer[1] starts from the Clausius-Clapeyron equation in the form

$$\frac{dp}{p} = \frac{L}{RT^2} \, dT \qquad \text{(IX.38)}$$

Writing this for two substances A and B and dividing the two equations for the case of a given temperature, he obtains

$$\frac{d \log p_A}{d \log p_B} = \frac{L_A}{L_B} \qquad \text{(IX.39)}$$

and by integrating this becomes

$$\log p_A = \frac{L_A}{L_B} \log p_B + C \qquad \text{(IX.40)}$$

When the log of the vapor pressure of several substances was plotted against that of a reference substance, straight lines were obtained the slope of which, according to the above equation, equals the ratio of the latent heats at a given temperature. Thus, if the latent heat of a reference material as a function of the temperature is known, it is possible to calculate that for other substances given two values of vapor pressure (one can be the normal boiling point).

Othmer[2] later presented a modification of his method that starts again with Eq. (IX.38) but introduces the critical state through the relations

$$p = p_c p_R$$
$$T = T_c T_R$$

and, by division at the same T_R, arrives at

$$\frac{d \ln p_R}{d \ln p_R'} = \frac{L T_c'}{L' T_c} \qquad \text{(IX.41)}$$

The ['] denotes a reference substance.

Integrating, $\qquad \log p_R = \frac{L T_c'}{L' T_c} \log p_R' + C \qquad \text{(IX.42)}$

[1] OTHMER, D. F., *Ind. Eng. Chem.*, **32**, 841 (1940).
[2] OTHMER, D. F., *Ind. Eng. Chem.*, **34**, 1072 (1942).

From available experimental data the integration constant C was shown to be zero.   Consequently, one can write

$$L = L' \frac{T_c \log p_R}{T_c' \log p_R'} \tag{IX.43}$$

p_R and p_R' are reduced vapor pressures of the substance in question and a reference substance, respectively, both at the same reduced temperature. The normal boiling point of the substance may be chosen for this point. L and L' are also for the same reduced temperature.   With the aid of this equation one can calculate latent heat at any temperature, given only the normal boiling point and the critical pressure and temperature.

Meissner[1] starts with the Clausius-Clapeyron equation, introduces the compressibility factors through the two volumes, assumes a linear log p vs. $1/T$ relation for vapor pressure to the critical point, and arrives at the equation

$$\ln p_R = \frac{L}{R(C_g - C_L)T_c}\left(1 - \frac{1}{T_R}\right) \tag{IX.44}$$

p_R and T_R are reduced vapor pressure and boiling point, respectively; C_g and C_L are compressibility factors of vapor and liquid, respectively. Since C_g and C_L can be represented as functions of p_R and T_R, L/T_c is a unique function of these two variables.   Meissner gives a graph of this function from which L may be determined if the vapor pressure and critical temperature of a substance are known.   Vapor pressures over the whole range may be estimated from two known values using the linear log p vs. $1/T$ relation.   This graph was used by Meissner to calculate L for a wide variety of liquids and of conditions, and comparison with experimental data showed an average deviation of less than 5 per cent with a maximum of only ± 9 per cent.

The use of the various methods will be illustrated in the following problem.

Illustration 5.—Calculate the latent heat of vaporization for the following cases: (1) ethyl alcohol at 0°C.; (2) ammonia at 100°C.; (3) n-butane at 240.2°F. (115.7°C.). The experimental values are, respectively, 10,110, 3,050, and 2,980 c.h.u. per lb.-mole. Data on the three compounds are as follows:

Substance	T_B, °K.	T_c, °K.	p_c, atm.	Vapor pressure, atm., at the temperature in question
EtOH	351.5	516.3	63.1	0.016
NH$_3$	240.0	405.5	111.5	61.8
n-C$_4$H$_{10}$	272.7	426.2	36.0	20.4

[1] Meissner, W., *Ind. Eng. Chem.*, **33**, 1440–1443 (1941).

Centigrade heat units, pounds-moles, atmospheres, and degrees Kelvin will be used throughout.

Kistiakowsky Method.—This is not strictly applicable to any of these cases but will be used in the case of ethyl alcohol to show how far off one can come if the limitations are not closely adhered to.

$$L = 273.2(8.75 + 4.571 \log_{10} 273.2) = 5,440$$

The error is nearly 50 per cent.

Use of Hildebrand Function.—By using the graph in the paper by McAdams and Morrell for benzene in the case of butane and for water in the case of ammonia, the following values are obtained:

Substance	$1000 \dfrac{p_{atm}}{T^\circ K.}$	$\dfrac{L}{T}$	L
EtOH	0.059	37	10,100
NH$_3$	165	12	4,470
n-C$_4$H$_{10}$	52	10.5	4,090

This method is good for low pressures but gives results that are much too high at high pressures.

Watson Method [combination of Eqs. (IX.36) and (IX.37)].—The constant B in

$$\ln p_{atm} = A - \frac{B}{T - 43} \qquad \text{[Eq. VI.59]}$$

will be evaluated from the normal boiling point and the critical point.

The equation for this is

$$B = \frac{2.303 \log_{10} (p_c/p_B)}{[1/(T_B - 43)] - [1/(T_c - 43)]}$$

Values of B, L_B, and L are as follows:

Substance	B	L_B	L
EtOH	3,690	9,050	10,500
NH$_3$	2,040	5,700	3,060
n-C$_4$H$_{10}$	2,130	5,650	3,300

The agreement is fairly good in all three cases.

Othmer Methods.—In using the first of Othmer's methods we shall calculate the latent heats of ethanol and butane only, using water as the reference substance for the former and ammonia for the latter. Water would not be suitable as the reference for either ammonia or butane if the normal boiling points are chosen as one of the known vapor pressures because the temperatures are too low. In addition to the normal boiling point we shall choose the vapor pressure at the temperature where the latent heat is to be determined. The values to be plotted on log-log coordinates will be as follows:

1. EtOH:

$$t = 78.3°C. \qquad p_{EtOH} = 760 \text{ mm.} \qquad p_{H_2O} = 332 \text{ mm.}$$
$$t = 0°C. \qquad p_{EtOH} = 12.2 \text{ mm.} \qquad p_{H_2O} = 4.58 \text{ mm.}$$

2. Butane:

$$t = -0.5°C. \qquad p_{C_4} = 760 \text{ mm.} \qquad p_{NH_3} = 4.23 \text{ atm.}$$
$$t = 115.7°C. \qquad p_{C_4} = 20.4 \text{ atm.} \qquad p_{NH_3} = 83.0 \text{ atm.}$$

As a matter of fact, it is easier to obtain the slopes from the relation

$$\text{Slope} = \frac{\Delta \log p_A}{\Delta \log p_B}$$

rather than to use a graph.

For ethanol,
$$\text{Slope} = \frac{2.881 - 1.086}{2.522 - 0.661} = 0.965$$

$$L \text{ for water at } 0°C. = 10,760$$
$$L \text{ for EtOH} = 0.965 \times 10,760 = 10,390$$

For butane,
$$\text{Slope} = 1.013$$
$$L \text{ for NH}_3 \text{ at } 115.7°C. \ (240°F.) = 2,160$$
$$L \text{ for butane} = 1.013 \times 2,160 = 2,190$$

The agreement is good in the case of alcohol but rather poor in the case of butane. Doubtless the agreement would have been better had another reference substance been used, but this illustrates one of the main difficulties of the method, *viz.*, the choice of a suitable reference liquid.

Othmer's second method [Eq. (IX 43)] will be illustrated in detail for the ethanol case and only the final result given for the other two.

$$T_R \text{ of ethanol at normal boiling point} = \frac{351.5}{516.3} = 0.680$$

$$p_R \text{ of ethanol at normal boiling point} = \frac{1}{63.1} = 0.01586$$

Since T_R (ethanol) $= T_R(H_2O)$,

$$T_{H_2O} = T_R T_c = 0.680 \times 647 \text{ [critical temperature of } H_2O \ (°K.)] = 440°K. = 333°F.$$

Vapor pressure of H_2O at 333°F. $= 7.31$ atm.

$$p_R(H_2O) = \frac{p}{p_c} = \frac{7.31}{217.7} = 0.0336$$

$$\frac{\log p_R}{\log p_R'} = \frac{-1.7997}{-1.4737} = 1.221$$

By Eq. (IX.43),
$$\frac{L}{L'} = \frac{516.3}{647} \times 1.221 = 0.977$$

At 0°C.,
$$T_R(\text{EtOH}) = \frac{273.2}{516.3} = 0.529 = T_R(H_2O)$$

$$T(H_2O) = 0.529 \times 647 = 342°K. = 155°F.$$
$$L \text{ of } H_2O \text{ at } 155°F. = 10,060$$
$$L \text{ of EtOH} = 0.977 \times 10,060 = 9,850$$

By the same method, one obtains

$$L \text{ of ammonia at } 100°C. = 3,080$$
$$L \text{ of } n\text{-butane at } 115.7°C. = 3,160$$

The agreement between calculated and experimental values is quite good in all three cases.

Meissner Method.—This method requires the vapor pressure at the point for which the latent heat is desired. In the absence of the vapor-pressure curve one might use the linear log p vs. $1/T$ relation, evaluating the two constants from the normal boiling point and one other point, which might be the critical point. For the present illustration we shall use the data taken from the literature that were given above. The values of reduced pressure and temperature for the three cases are given in the first two columns of the following table. The third column gives the value read from Meissner's graph and the last column the calculated value of L.

Substance	p_R	T_R	$\dfrac{L}{T_c}$	L
EtOH	2.54×10^{-4}	0.529		
NH_3	0.555	0.920	7.4	3,000
$n\text{-}C_4H_{10}$	0.566	0.912	6.2	2,640

In the case of EtOH, the pressure is so low that $C_g - C_L$ in Eq. (IX.44) $= 1.00$ and L can be calculated directly without using the graph. The result is 9,550. In all three cases the agreement with experiment is good.

Heat of Fusion.—This enthalpy difference can be calculated from freezing-point data on solutions by applying Eq. (IV.206) in the form

$$\Delta H_A = RT^2 \left(\frac{\partial \ln \dfrac{x''}{x'}}{\partial T} \right)_p \tag{IX.45}$$

where x'' is the mole fraction of A in the liquid phase and x' is the same for the solid phase. The equation assumes an ideal solution in both phases. Assuming ΔH_A to be a constant, we can obtain

$$\ln \frac{x''}{x'} = - \frac{\Delta H_A}{RT} + C \tag{IX.46}$$

According to this equation a graph of $\ln x''/x'$ vs. $1/T$, the reciprocal of the freezing point, will give a straight line the slope of which is $-\Delta H_A/R$.

For the case where the solid phase is the pure component or where the solid solution contains only a small concentration of one component, Eq. (IX.46) becomes

$$\ln x'' = - \frac{\Delta H_A}{RT} + C \tag{IX.47}$$

Kelley[1] made extensive use of these equations to calculate the latent heat of fusion of inorganic substances. Equation (IX.47) is also useful for the calculation of the solubility of a pure solid component in an ideal-liquid solution when the heat of fusion is known.

[1] KELLEY, K. K., *U.S. Bur. Mines Bull.* 393 (1936).

Enthalpy of Solutions. *Constant Composition.*—The case of a solution, heated or cooled at constant composition, is substantially the same as that of a single component. Of course, one needs data on the heat capacity of the solution, and it would be desirable to calculate these from the heat capacities of the pure components; but little progress has been made in this direction, and one must resort to experimental values. Since heat capacity is an extensive property, the general relation for such a property applies and for this special case becomes

$$C_p = \bar{C}_{p_A} N_A + \bar{C}_{p_B} N_B + \cdots$$

(heat capacity at constant pressure is the only one that will be considered in this discussion), or, for heat capacity per mole or unit mass,

$$C_p = \bar{C}_{p_A} x_A + \bar{C}_{p_B} x_B + \cdots \qquad \text{(IX.48)}$$

The partial quantities are functions of temperature, the nature of the component, and the composition of the solution and, to a lesser extent, of the pressure. For an ideal solution it is evident from Eq. (IV.116) that

$$\bar{C}_{p_i} = C_{p_i}$$

which means that $\bar{C}_p$ is independent of composition. Consequently, for this special case the specific heat of a solution is very simply calculated from the specific heats of the pure components. For nonideal solutions we have no way at the present time of calculating the specific heat. The assumption of ideal solution would be a satisfactory approximation in some cases, but it may lead to quite erroneous results in others. For example, in the case of nitric acid–water solutions, the partial specific heats can be calculated from available data on the specific heat of the solutions, and the results show that the partial specific heat of the water at room temperature varies from a minimum of 0.76 to a maximum of 1.42. Until someone develops a method for calculating the partial specific heats from something other than specific-heat data on the given solution, they are entirely useless because if one has such data he does not need the partial quantities. The same thing is more or less true of all the partial quantities at the present time, and there has been some tendency on the part of many writers to exaggerate their importance.

Heats of Solution and Dilution.—There are many important industrial operations in which solutions are either produced from the components, mixed, diluted, or concentrated, such changes involving a heat effect along with a change in concentration. In this section, we shall be concerned with such heat effects and more particularly with their relation to composition and temperature.

When two pure liquids, for example, alcohol and water, or a soluble solid and a liquid, such as a salt and water, are mixed, there is a heat

effect that may be either positive (heat evolved) or negative (heat absorbed). If the two components are at the same temperature and the solution formed is brought to this same temperature so that the over-all process is isothermal, the heat effect is known as the "integral heat of solution" or simply as the "heat of solution." In order to be a definite quantity it must be based on a given mass either of one of the components or of the solution. Usually, when one of the components is a solid, a unit or molal mass of that component is chosen; when both are liquids, it is more common to base the heat of solution on a unit or molal mass of solution. This quantity is, in general, a function of the pressure, the
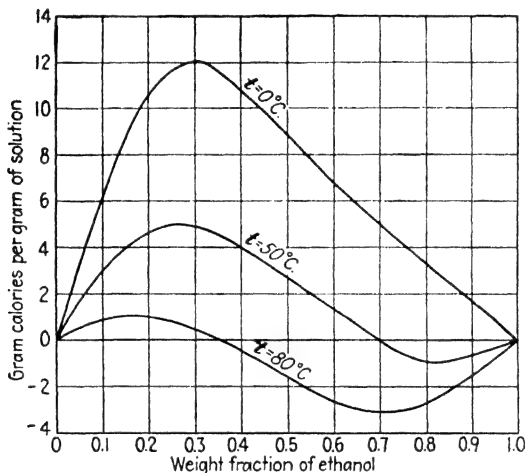
FIG. IX.4 — Integral heat of solution of ethanol-water mixtures as a function of temperature and composition.

temperature, and the concentration of solution formed. Most heats of solution have been determined at a standard pressure of 1 atm. and a standard temperature of either 18 or 25°C. The effect of pressure can usually be ignored because it is very small in the case of liquids and in the case of gases the heat of solution is a minor effect except at very high pressures.

Variation of integral heat of solution with temperature is illustrated by some data for ethanol-water solutions given in Fig. IX.4.

Per mole of solute, heats of solution may run as high as 20,000 g.-cal., in other words, may be of the same order as many heats of chemical reaction. In many cases, chemical reaction or something closely akin to it does occur in the solution process. In dealing with cases such as the formation of sulphuric acid solutions or oleums from SO_3 and water it is convenient to treat them as if they were purely physical solution processes and to ignore the reaction.

When one of the components is added to a solution already formed, the heat effect for the isothermal process is called a "heat of dilution." It is obvious that the difference between any two heats of solution for two different concentrations is simply the heat of dilution between those two concentration limits (referred, of course, to a common mass basis). In fact, heats of solution are usually measured by determining the heat effect in the formation of a concentrated solution from the two pure components and thereafter measuring heats of dilution.

When a differential amount of either component is added to a solution of the two so that the concentration of the solution changes only a differential amount, the heat effect for this case is called a "differential heat of solution."
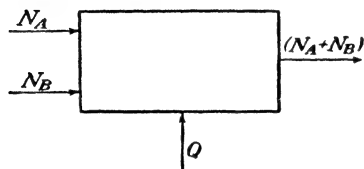
Fig. IX.5.—Integral heat of solution.

Since heats of solution or dilution are heat effects at constant pressure, they can be represented as enthalpy differences. A relation between the enthalpy of a solution, the enthalpies of the two pure components, and the integral heat of solution may be very simply obtained by considering the continuous mixing process illustrated in Fig. IX.5. Applying the first law, we have

$$N_A H_A + N_B H_B - Q = (N_A + N_B)H_s \qquad (IX.49)$$

where N_A = moles of component A.

N_B = moles of B.

H_A = molal enthalpy of pure A at the given pressure and temperature.

H_B = same for B.

Q = heat effect for the isothermal process (positive for heat evolved).

H_s = enthalpy of the solution produced.

Dividing by N_A and rearranging,

$$H_s = x H_A + (1 - x)H_B - x q_A \qquad (IX.50)$$

where q_A is the integral heat of solution per mole of component A and x is the mole fraction of A.

Similarly, we can get

$$H_s = x H_A + (1 - x)H_B - q_s \qquad (IX.51)$$

where q_s is the integral heat of solution per mole of solution. These equations permit the calculation of enthalpy of solutions along an isotherm from measurements of integral heat of solution. In dealing with any physical process, the enthalpies of individual components can be chosen

quite independently, and it is convenient to choose both H_A and H_B equal to zero at a base, or reference, isotherm. In some cases, enthalpy data on solutions and on the two pure components are already available on different bases, and the problem is one of relating them. This is very simply accomplished by applying Eq. (IX.51) at some state for which the heat of solution is known or where it can be assumed equal to zero. This will give a calculated H_s, and the difference between calculated and tabulated values of H_s is a constant and can be applied as a correction factor for the entire region of the data.

Illustration 6.—A tabulation of the thermodynamic properties of air has been recently published.[1] It is desired to find a correction factor to apply to the enthalpy data in this tabulation to put them on the same basis as the oxygen and nitrogen data of Millar and Sullivan[2] so that the three sets of data can be used together in a given problem.

At a pressure of 1 atm. and a temperature around that of the room, air can be regarded as an ideal solution.

$$\therefore H_{\text{air}} = 0.21 H_{O_2} + 0.79 H_{N_2} \qquad (1)$$

at a given pressure and temperature.

At $T = 500°$R. and $p = 1$ atm., H_{air} from the Williams table = 220.1 B.t.u. per lb., or $220.1 \times (29/1.8)$ C.h.u. per lb.-mole = 3,550. The values for O_2 and N_2 at the same condition and in the same units are

$$H_{O_2} = 3,094$$
$$H_{N_2} = 2,727$$

Substituting in (1), $\qquad H_{\text{air}} = 2,808$

The correction = $3,550 - 2,808 = 742$. In other words, any enthalpy in the Williams table can be placed on the basis of the Millar-Sullivan tables by subtracting 742 from the value in centigrade heat units per pound-mole, or $(742 \times 1.8)/29 = 46.0$ from the actual tabulated values in B.t.u. per pound.

If the mixing process of Fig. IX.5 is carried out with only a differential amount of A, dN_A, the heat effect would be the differential heat of solution. The quantitative relation is simply obtained by differentiating Eq. (IX.49) with respect to N_A, giving

$$\left(\frac{\partial Q}{\partial N_A}\right)_{T,N_B} = \bar{q}_A = H_A - H_s - (N_A + N_B)\left(\frac{\partial H_s}{\partial N_A}\right)_{T,N_B} \qquad (IX.52)$$

Eliminating dN_A through the relation

$$dN_A = (N_A + N_B)\frac{dx}{1 - x}$$

one gets $\qquad \bar{q}_A = H_A - H_s - (1 - x)\left(\frac{\partial H_s}{\partial x}\right)_T \qquad (IX.53)$

[1] Williams, V. C., *Trans. Am. Inst. Chem. Eng.*, **39**, 93–111 (1943).
[2] Millar and Sullivan, *op. cit.*

Differentiating Eq. (IX.51)

$$\left(\frac{\partial H_s}{\partial x}\right)_T = -\left(\frac{\partial q_s}{\partial x}\right)_T + H_A - H_B \tag{IX.54}$$

Combining Eqs. (IX.51), (IX.53), and (IX.54),

$$\bar{q}_A = q_s + (1 - x)\left(\frac{\partial q_s}{\partial x}\right)_T \tag{IX.55}$$

Equation (IX.55) could have been obtained directly from the general equations for extensive properties given in Chap. IV. Thus, if the property is enthalpy, it follows at once that

$$\bar{H}_A = H_s + (1 - x)\left(\frac{\partial H_s}{\partial x}\right)_T \tag{IX.56}$$

and

$$\bar{H}_B = H_s - x\left(\frac{\partial H_s}{\partial x}\right)_T \tag{IX.57}$$

Equation (IX.55) is derivable by inspection from Eq. (IX.56) since a heat of solution is merely a difference of two enthalpies.

Since

$$q_s = \bar{q}_A x + \bar{q}_B(1 - x) \tag{IX.58}$$

Eq. (IX.51) can be changed to

$$H_s = x H_A + (1 - x)H_B - \bar{q}_A x - \bar{q}_B(1 - x) \tag{IX.59}$$

Figure IX.6 shows graphically on an enthalpy-concentration diagram the relationship between several of the quantities that have just been discussed. ABC is an isotherm relating the enthalpy to the concentration of component A in a binary solution. From Eq. (IX.51) it is evident that BD is q_s, the integral heat of solution per mole of solution for the solution of composition x_1; it is positive (heat evolved) in this case. EF is drawn tangent to the isotherm at x_1; and therefore, for a solution of this composition, AE is the differential heat of solution of component B, and CF is the same for component A. This is readily seen from the following considerations based on Fig. IX.6.

The slope of EF is $\overline{BG}/\overline{EG}$, and $\overline{BG}/\overline{EG} = \overline{BG}/x_1$.

Therefore, at x_1,

$$x_1\left(\frac{\partial H_s}{\partial x}\right)_T = \overline{BG}$$

$$H_s - \overline{BG} = \overline{EO} = \bar{H}_B \qquad \text{[by Eq. (IX.57)]}$$

But, by Eqs. (IX.53) and (IX.56),

$$\bar{q}_A = H_A - \bar{H}_A \tag{IX.60}$$

and similarly

$$\bar{q}_B = H_B - \bar{H}_B \tag{IX.61}$$

Therefore, since

$$\overline{AO} - \overline{EO} = \overline{AE}$$

then

$$H_B - \bar{H}_B = \overline{AE} = \bar{q}_B$$

A diagram such as Fig. IX.6 assumes complete miscibility over the entire composition range from pure B to pure A. In the case where A is a solid, there will be limited miscibility and the isotherms such as ABC would end at the composition of the saturated solution.

The use of Eq. (IX.51) for calculation of enthalpy of solution implies that the reference state for both components is the pure substance. It may not always be convenient to choose this reference state; for example, if one has data on heat of dilution but not on heat of solution, there would be no way to proceed from the state of pure A to that of any solution. In such cases it is common practice to choose an infinitely dilute
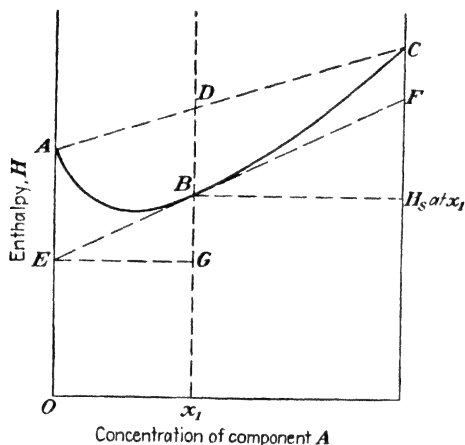
Fig. IX.6.—Relations between enthalpies and heats of solution. (At the origin, $x = 0$ and $H = 0$.)

solution as the reference state for the solute, A, and to let $\bar{H}_A = 0$ for this solution at some one base temperature.

To derive an equation analogous to Eq. (IX.51) for this case we shall proceed as follows:

Consider an initial solution containing N_A moles of A and N_B of B, whose molal enthalpy is H_s. Add solvent to dilute the solution to one containing N'_B moles of B. From the first law,

$$Q_D = (N_A + N_B)H_s + (N'_B - N_B)H_B - (N_A + N'_B)H'_s \quad \text{(IX.62)}$$

where Q_D = total heat of dilution.

Utilizing the fact that

$$(N_A + N'_B)H'_s = N_A\bar{H}'_A + N'_B\bar{H}'_B \quad \text{(IX.63)}$$

Eq. (IX.62) becomes

$$Q_D = (N_A + N_B)H_s + N'_B H_B - N_B H_B - N_A\bar{H}'_A - N'_B\bar{H}''_B \quad \text{(IX.64)}$$

If the final state is one of infinite dilution,

$$Q_D = Q_\infty$$

and

$$\bar{H}'_B = H_B$$

Making these substitutions in Eq. (IX.64),

$$Q_\infty = (N_A + N_B)H_s - N_A\bar{H}'_A - N_B H_B \qquad (IX.65)$$

Now if we choose the reference state of A as the infinitely dilute solution and let

$$\bar{H}'_A = 0$$

at a standard temperature, we get

$$Q_\infty = (N_A + N_B)H_s - N_B H_B \qquad (IX.66)$$

or, basing the heat of infinite dilution on 1 mole of the solute A, Eq. (IX.66) can be written

$$q_\infty = \frac{Q_\infty}{N_A} = \frac{H_s}{x} - \frac{1-x}{x}H_B \qquad (IX.67)$$

or

$$H_s = xq_\infty + (1-x)H_B \qquad (IX.68)$$

The heat of infinite dilution can be obtained by plotting the heat of solution per mole of solute against the number of moles of solvent added. The curve will approach a horizontal asymptote which is q_∞. A better method of extrapolating heat of solution data was demonstrated by Rossini,[1] who showed that the Debye-Hückel theory leads to the following limiting law as the concentration approaches zero:

$$q_D = \alpha \sqrt{c}$$

where q_D = heat of dilution from a given concentration c to an infinitely dilute solution, per mole of solute.

  α = a constant that equals 435 for uni-univalent electrolytes at 18°C., when q_D is in centigrade heat units per pound-mole and c in molality.

By plotting the experimental data on q_D vs. $\sqrt{c}$, the straight line representing the limiting law guides the extrapolation to $c = 0$.

Illustration 7.—One hundred pounds of an oleum solution containing 15.4 per cent free SO_3 is to be diluted with pure water to make a 30.8 per cent solution of H_2SO_4 in water. How much heat is evolved if the initial and final temperatures are the same and approximately 18°C.?

This problem was solved by Morgen [*Ind. Eng. Chem.*, **34**, 571–574 (1942)] using partial molal quantities. It will be solved here directly with the integral heat of solution data, which will be taken from his paper.

[1] ROSSINI, F. D., *Bur. Standards J. Research*, **6**, 791 (1931).

Basis: 100 lb. of oleum.

$$\text{Moles of } SO_3 = \frac{15.4}{80} + \frac{84.6}{98} = 1.057$$

$$\text{Moles of } H_2O = \frac{84.6}{98} = 0.860$$

Mole fraction of SO_3 = 0.55

Mole fraction of SO_3 in final solution

$$= \frac{(30.8/98)}{(30.8/98) + (69.2/18) + (30.8/98)} = 0.070$$

$$\text{Total moles of final solution} = \frac{1.057}{0.070} = 15.09$$

From the table in Morgen's paper, the integral heat of solution data are as follows:

Mole Fraction of SO_3	q_s, B.t.u./Lb.-mole
0.55	18,200
0.07	4,720

The heat evolved is simply the difference between the total heats of solution of the initial and final solutions.

$$\therefore \text{ Heat evolved} = 15.09 \times 4{,}720 - 1.917 \times 18{,}200$$
$$= 36{,}400 \text{ B.t.u.}$$

This method is a good deal simpler than the one using partial quantities and probably more accurate since it does not depend on the measurement of slopes.

Illustration 8.—A 23.2 per cent H_2SO_4 solution (solution 1) is to be fortified to 80.6 per cent H_2SO_4 (solution 3) by addition of an oleum (solution 2) containing 41.2 per cent free SO_3. How much heat must be removed per 100 lb. of initial acid to bring the temperature back to its initial value of 18°C.? (Same as Morgen's example 2.[1])

Let Q_1 = heat effect for the isothermal formation of solution 1 from the components SO_3 and H_2O.

Q_2 = heat effect for the isothermal formation of solution 2.

Q_3 = heat effect from mixing solutions 1 and 2 to form solution 3.

Q_4 = integral heat of solution for solution 3.

Since these heat effects are all values of ΔH, the formation of solution 3 from the components through the intermediate steps of forming solutions 1 and 2 and then mixing these to form solution 3 must give the same heat effect as the direct formation of solution 3 from the components.

$$\therefore Q_1 + Q_2 + Q_3 = Q_4 \tag{1}$$

Take a mass basis of 100 lb. of solution 1.

$$\text{Moles of solution 1} = \frac{23.2}{98} \times 2 + \frac{76.8}{18} = 4.738$$

The mole fraction of SO_3 in each solution is readily obtained, as shown in Illustration 7, with the following results:

	Solution 1	Solution 2	Solution 3
Mole fraction of SO_3 =	0.050	0.650	0.302

[1] MORGEN, R. A., *Ind. Eng. Chem.*, **34**, 571–574 (1942).

Let N = moles of oleum added.

An SO_3 balance gives

$$4.738 \times 0.050 + 0.650N = 0.302(N + 4.738)$$
$$N = 3.43$$

From the table in Morgen's paper, the three heats of solution per mole of solution are as follows:

$$\Delta H_1 = -3,400$$
$$\Delta H_2 = -15,330$$
$$\Delta H_4 = -15,800$$

Applying (1),

$$Q_3 = 15,800 \times 8.167 - 3,400 \times 4.738 - 3.43 \times 15,330 = 60,350 \text{ B.t.u.}$$

Heat of Vaporization.—The latent heat of vaporization of a binary solution may be either differential or integral. The former is the heat effect for the vaporization of a differential amount of the liquid to produce the equilibrium vapor and is directly related to the vapor pressure of the solution, as shown in Chap. IV. Thus, with Eq. (IV.155) the differential latent heat could be calculated, given data on the vapor pressure of the solution at constant composition and on the partial volumes of the two phases. For an ideal solution, Eq. (IV.187) applies and for this special case can be written

$$L \text{ (differential)} = L_A y + L_B(1 - y) \tag{IX.69}$$

The integral heat is that for complete vaporization of the liquid at constant composition and there are two of them, one for a constant-pressure process and the other for constant temperature. The remainder of our discussion will be concerned only with the former. It may be related to other quantities as follows:

For the vapor and liquid, respectively,

$$H_s = y\bar{H}_A + (1 - y)\bar{H}_B \tag{IX.70}$$
$$h_s = x\bar{h}_A + (1 - x)\bar{h}_B \tag{IX.71}$$

Let $H_s - h_s = L_{p,x}$, the integral latent heat of vaporization at constant pressure and composition.

Noting that $y = x$, one can write

$$L_{p,x} = x(\bar{H}_A - \bar{h}_A) + (1 - x)(\bar{H}_B - \bar{h}_B) \tag{IX.72}$$

By Eq. (IX.60) $\quad \bar{H}_A = H_A - \bar{q}_A'' = H_{A_0} + \int_{T_{A_0}}^{T_1} C_{p_A}'' \, dT - \bar{q}_A'' \tag{IX.73}$

T_{A_0} is the boiling point of pure A at the pressure of the solution, and T_1 is the dew-point temperature of the solution. C_{p_A}''' is the specific heat of pure A in the vapor, and $\bar{q}_A''$ is the differential heat of mixing of A in the vapor.

An analogous equation for the liquid is

$$\bar{h}_A = h_{A_0} + \int_{T_{A_0}}^{T_2} C'_{p_A} \, dT - \bar{q}'_A \tag{IX.74}$$

where T_2 is the bubble-point temperature.

Subtracting Eq. (IX.74) from Eq. (IX.73) and noting that

$$L_{A_0} = H_{A_0} - h_{A_0},$$

we have

$$\bar{H}_A - \bar{h}_A = L_{A_0} + \int_{T_{A_0}}^{T_2} (C''_{p_A} - C'_{p_A}) \, dT + \int_{T_2}^{T_1} C''_{p_A} \, dT + \bar{q}'_A - \bar{q}''_A \tag{IX.75}$$

with a similar equation for component B.

Substitution of Eq. (IX.75) and the analogous equation for B into Eq. (IX.72) and use of Eq. (IX.58) and its analogous equation for the vapor lead to

$$
\begin{aligned}
L_{p,x} = L_{A_0}x &+ L_{B_0}(1 - x) + x \int_{T_{A_0}}^{T_2} (C''_{p_A} - C'_{p_A}) \, dT \\
&+ (1 - x) \int_{T_{B_0}}^{T_2} (C''_{p_B} - C'_{p_B}) \, dT + x \int_{T_2}^{T_1} C''_{p_A} \, dT \\
&+ (1 - x) \int_{T_2}^{T_1} C''_{p_B} \, dT + q'_s - q''_s \quad (\text{IX.76})
\end{aligned}
$$

We can assume the vapor to be an ideal solution without introducing appreciable errors, and this leads to

$$C''_p = xC''_{p_A} + (1 - x)C''_{p_B}$$
$$q''_s = 0$$

Furthermore, the temperature ranges are so small that all C_p's can be considered constant. With these assumptions, Eq. (IX.76) becomes

$$
\begin{aligned}
L_{p,x} = L_{A_0}x &+ L_{B_0}(1 - x) + q'_s + x(C''_{p_A} - C'_{p_A})(T_2 - T_{A_0}) \\
&+ (1 - x)(C''_{p_B} - C'_{p_B})(T_2 - T_{B_0}) + C''_p(T_1 - T_2) \quad (\text{IX.77})
\end{aligned}
$$

From this equation one can calculate the latent heat of the solution from the latent heats of the pure components, the specific heats of the pure components, and the integral heat of solution. If the solution is ideal, $q'_s = 0$; and finally, if the specific-heat terms are neglected since they are small compared with the latent heats, one has, as a first approximation,

$$L_{p,x} = L_{A_0}x + L_{B_0}(1 - x) \tag{IX.78}$$

There are very few data for either testing or applying these relationships. Even though they cannot be applied exactly in many cases, they are still useful for approximations and qualitative deductions. For example, Eq. (IX.77) shows that the latent heat of vaporization of a solution

is approximately equal to the sum of the heats of vaporization of the components plus the integral heat of solution.

For the case of a solution of a nonvolatile solute, one can derive in a similar way, the equation

$$L_B = h_{B0} + L_{B0} + \int_{t_B}^{t_2} C''_{pB}\, dt + \frac{x_1}{x_2 - x_1}[x_2 h_{A2} + (1 - x_2)h_{B2} - x_2 q_2]$$
$$- \frac{x_2}{x_2 - x_1}[x_1 h_{A1} + (1 - x_1)h_{B1} - x_1 q_1] \quad \text{(IX.79)}$$

where L_B = latent heat of vaporization at constant pressure, of solvent from a solution of mole fraction x_1 to produce a solution of mole fraction x_2.

h_{B0} = enthalpy of pure liquid B (solvent) at its boiling point, T_B.

L_{B0} = latent heat of vaporization of pure B at the pressure over the solution.

C''_{pB} = molal heat capacity of vapor of B.

h_{A2} = enthalpy of solute at the boiling point of solution 2.

h_{B2} = enthalpy of solvent at the boiling point of solution 2.

h_{A1} and h_{B1} = analogous quantities for solution 1.

q_2 = integral heat of solution for solution 2 per mole of solute.

q_1 = integral heat of solution for solution 1 per mole of solute.

The vapor of solvent is assumed to leave at the final temperature, T_2. If we neglect differences in sensible heats, Eq. (IX.79) reduces to

$$L_B = L_{B0} + \frac{x_1 x_2}{x_2 - x_1}(q_1 - q_2) \quad \text{(IX.80)}$$

which is sufficiently accurate for most purposes.

Enthalpy of Solutions from Vapor-pressure or Electromotive-force Data.— If one has only a limited amount of data on heats of solution or dilution, it is possible to fill in gaps by utilizing vapor-pressure data. From Chap. IV,

$$\left(\frac{\partial \ln \bar{a}_i}{\partial T}\right)_{p,x} = -\frac{\bar{H}_i - \bar{H}_i^\circ}{RT^2} \quad \text{(IV.110)}$$

Replacing $\bar{a}_i$ by f_i/f_i° and noting that $\bar{f}_i^\circ = f_B$ if one is dealing with the solvent and the standard state is that of pure liquid solvent, Eq. (IV.110) becomes

$$d \ln \frac{\bar{f}_B}{f_B} = -\frac{\bar{H}_B - H_B}{RT^2}\, dT \quad \text{(IX.81)}$$

or, for ideal gases,

$$d \ln \frac{\bar{p}_B}{p_B} = -\frac{\bar{H}_B - H_B}{RT^2}\, dT \quad \text{(IX.82)}$$

From a plot of $\ln (\bar{p}_B/p_B)$ vs. T at constant x, one can determine the slopes and hence $\bar{H}_B - H_B$ along an isotherm. $\bar{H}_B$ is then obtained

from known values of H_B. From $\bar{H}_B$ one can obtain $\bar{H}_A$ by use of the usual relation for partial quantities [see Eq. (IV.9)], which, for this case, becomes

$$\int d\bar{H}_A = -\int \frac{1-x}{x} d\bar{H}_B \qquad (IX.83)$$

The enthalpy of the solution is then very easily obtained from Eq. (IX.70) or (IX.71). For an illustration of the use of vapor-pressure data to calculate enthalpy of a solution, reference may be made to a paper by Haltenberger,[1] who calculated several enthalpy-concentration isotherms for sodium hydroxide solutions using the Dühring relation for obtaining vapor pressures. Enthalpy of solution of ionizable solutes can be obtained from e.m.f. measurements on suitable electrochemical cells. From the e.m.f. data, the activity of the solute can be calculated and then Eq. (IV.110) applied to obtain the enthalpy difference $\bar{H}_i - \bar{H}_i^{\circ}$, or relative partial molal enthalpy as it is commonly called. Such data on HCl solutions at temperatures from 0 to 50°C. and for concentrations up to 16 molal were obtained by Akerlof and Teare[2] and used by them to calculate various thermodynamic properties, including the above-mentioned enthalpy difference.

THE ENTHALPY-CONCENTRATION DIAGRAM

Application to Mixing Problems.—When a number of problems involving heat effects accompanying concentration changes of a given binary solution are to be solved, an enthalpy-concentration diagram proves to be very convenient. It has been called a "Merkel diagram" by some writers, after the German engineer[3] who applied it to problems in heat effects accompanying solutions. It is also associated with the names

Fig. IX.7.—Simple mixing process.

of Ponchon[4] and Savarit,[5] who applied it to problems in distillation. The most complete development of its use is undoubtedly due to Bosnjakovic,[6] whose excellent treatise should be consulted for many more applications than can be given here.

Before considering in detail the construction of such a diagram, let us review briefly some of its properties. Consider the simple continuous

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[1] HALTENBERGER, W., JR., *Ind. Eng. Chem.*, **31**, 783–786 (1939).

[2] AKERLOF, G., and J. TEARE, *J. Am. Chem. Soc.*, **59**, 1855 (1937).

[3] MERKEL, F., *Z. Ver. deut. Ing.*, **72**, 109 (1928); *Zeit. ges. Kälte-Ind.*, **35**, 130 (1928).

[4] PONCHON, M., *Tech. Moderne*, **13**, 20–24, 55–58 (1921).

[5] SAVARIT, R., *Arts et métiers*, pp. 65, 142, 178, 241, 266, 307 (1922).

[6] BOŠNJAKOVIĆ, F., "Technische Thermodynamik," Vols. 1 and 2, T. Steinkopf, Leipzig, 1935.

mixing process represented by Fig. IX.7, and make the three following balances for the case of an adiabatic process:

$$N_1 + N_2 = N_3 \quad \text{(IX.84)}$$
$$N_1 x_1 + N_2 x_2 = N_3 x_3 \quad \text{(IX.85)}$$
$$N_1 H_1 + N_2 H_2 = N_3 H_3 \quad \text{(IX.86)}$$

Either weights and weight fractions or moles and mole fractions may be used. Elimination of the three masses yields the equation

$$\frac{x_3 - x_1}{x_2 - x_1} = \frac{H_3 - H_1}{H_2 - H_1} \quad \text{(IX.87)}$$

This equation is represented as a straight line on a diagram whose coordinates are H and x, passing through the three points (H_1, x_1), (H_2, x_2),

Fig. IX.8.—Fundamental property of an enthalpy-concentration diagram.

and (H_3, x_3) as shown in Fig. IX.8. The proof of this proposition is very simply obtained from the principle of similar triangles.

Consider next the case of a nonadiabatic mixing process. The first two balance equations remain the same, but the third becomes

$$N_1 H_1 + N_2 H_2 = N_3 H_3 + Q \quad \text{(IX.88)}$$

Let $q_3 = Q/N_3$, the heat effect per unit of stream 3. Equation (IX.88) can then be written

$$N_1 H_1 + N_2 H_2 = N_3 H_3' \quad \text{(IX.89)}$$

where $H_3' = H_3 + q_3$.

Equation (IX.89) is now of the same form as Eq. (IX.86), and it is clear that the set of three equations (IX.84), (IX.85), and (IX.89) is also represented by a straight line on an Hx diagram connecting the three points (H_1, x_1), (H_2, x_2), and (H_3', x_3) (see Fig. IX.9). If we had chosen to base the heat effect on a unit of stream 1, the straight line would connect the points (H_1', x_1), (H_2, x_2), and (H_3, x_3) where

$$H_1' = H_1 - q_1 = H_1 - \frac{Q}{N_1}.$$

Fig. IX.9.—Use of enthalpy-concentration diagram to obtain the heat effect of a nonadiabatic process.

An actual Hx diagram will, of course, have a series of isotherms drawn on it so that any state point is readily located once the temperature and concentration of a solution are known. To make clear the fundamental

property of the diagram, which is the straight-line construction shown in Fig. IX.9, all other lines have been omitted. It also should be clear that a given Hx diagram is for one constant pressure.

Referring to Fig. IX.8, if the temperature and concentrations of solutions 1 and 2 are known, points 1 and 2 are located on the diagram and then point 3 is located since x_3 is readily calculated. Consequently, the temperature resulting from adiabatic mixing is very easily obtained
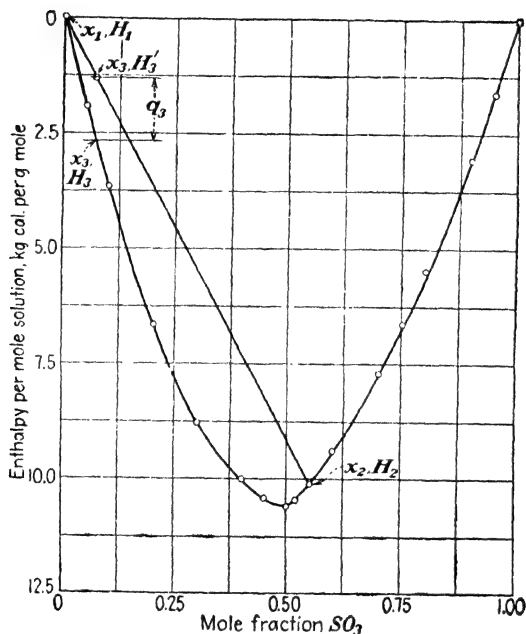
FIG. IX.10.—Solution of Illustration 9.

from the straight line. For a nonadiabatic process, the straight line now locates the point (x_3, H_3') and if the temperature of the mixture is known (for example, an isothermal process might be under consideration) point (x_3, H_3) is also located and from these q_3 is at once obtained as shown.

Illustration 9.—Solve Illustration 7 by means of a graphical construction on an enthalpy-concentration diagram.

Since only one isotherm is involved and since the enthalpy of both components can be arbitrarily made equal to zero, the diagram for this case (Fig. IX.10) is simply a graph of the integral heats of solution vs. concentration. The isotherm was plotted from the data in Morgen's paper.[1] The straight line connects the points $x_1 = 0$, $H_1 = 0$ (pure water) and $x_2 = 0.55$, $H_2 = 10,100$. H_3 and H_3' are located as shown

[1] MORGEN, R. A., *Ind. Eng. Chem.*, **34**, 571–574 (1942).
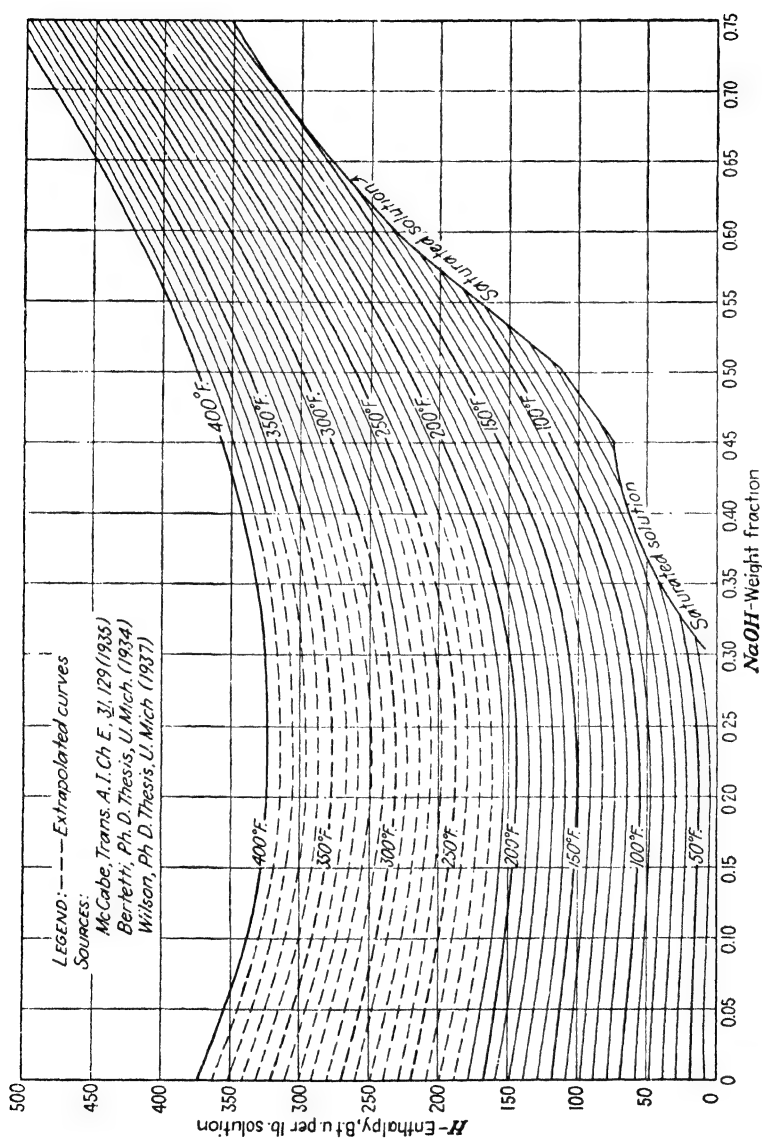
FIG. IX.11.—Enthalpy-concentration diagram for sodium hydroxide solutions. (Reproduced from a blueprint lent by Dr. W. L. McCabe. The original drawing of the diagram is due to Dr. R. York of Carnegie Institute of Technology.)

and their difference $q_3 = 1.35$ kg.-cal. per g.-mole of final solution. Since $N_3 = 15.09$, $Q = 15.09 \times 1.35 \times 1,800 = 36,600$ B.t.u.

Illustration 10.—1. Twelve hundred pounds of a 55 per cent by weight solution of NaOH at 100°F. is mixed with 400 lb. of a 15 per cent solution at 210°F. and the resulting solution cooled to 90°F. How much heat must be removed in the process? **2.** What would be the final temperature of the mixture if the process were adiabatic?

Use will be made of an enthalpy-concentration diagram for sodium hydroxide solutions furnished by McCabe,[1] which is reproduced in Fig. IX.11. The reference states for this diagram are $H = 0$ for water at 32°F. and $\bar{H} = 0$ for NaOH in the infinitely dilute solution at 68°F. The concentration of the final mixture, x_3, is obtained from an NaOH balance.

$$1,600x_3 = 1,200 \times 0.55 + 400 \times 0.15$$
$$x_3 = 0.450$$

From the chart the following values of enthalpy are read:

$$H_1 \text{ (55 per cent solution)} = 181 \text{ B.t.u./lb.}$$
$$H_2 \text{ (15 per cent solution)} = 156 \text{ B.t.u./lb.}$$
$$H_3 \text{ (final mixture)} = 110 \text{ B.t.u./lb.}$$

The solution of part (1) can be made by the graphical method already described or perhaps more easily by the use of the following equation readily obtained by elimination of the masses from Eqs. (IX.84), (IX.85), and (IX.88):

$$q_3 = H_1 - H_3 + (H_2 - H_1)\frac{x_3 - x_1}{x_2 - x_1}$$

Substituting values,

$$q_3 = 64.7 \text{ B.t.u. evolved per pound of final solution}$$
$$\therefore Q = 1,600 \times 64.7 = 103,500 \text{ B.t.u.}$$

2. This part can also be done just about as easily by the equation as by the graphical method.

Substituting in Eq. (IX.87)

$$H_3 = 174.7$$

In Fig. IX.11 the point whose coordinates are $x_3 = 0.45$, $H_3 = 174.7$ lies on the $t = 170°$F. isotherm, and therefore this is the desired temperature of the final solution.

A number of other applications of enthalpy-concentration diagrams will be given in Chap. XIII.

Construction of an Enthalpy-concentration Diagram.—As we have seen, it is quite simple to solve certain mixing problems once an enthalpy-concentration diagram (or the equivalent data in tabular form) is available, but unfortunately there are very few of them extant at the present time. It is desirable, therefore, to outline the method of construction and show the kinds of data that are needed.

The method of construction of such a diagram depends somewhat on the data available for the system in question. Let us first consider a system of two completely miscible liquids A and B (ethanol and water,

[1] Kindly loaned by Dr. W. L. McCabe of Carnegie Institute of Technology.

for example) and assume that the diagram is to apply only to the liquid region.   Assume that the available data are

1. Integral heats of solution and dilution for one isotherm, say 70°F.

2. Specific heats of the pure components and several different solutions as a function of temperature.

Choose both H_A and $H_B = 0$ at some one temperature, for example, 32°F.   Then locate the two terminal points on the base isotherm (the one at which heats of solution are available) from the relation

$$H_{t_0} = \int_{32}^{t_0} C_p \, dt \qquad (IX.90)$$

$H_{32} = 0$ for both components, by definition.

t_0 = temperature of the base isotherm, °F.

This locates points A and B in Fig. IX.12.   From the heat of solution data, calculate H_s by Eq. (IX.51) and plot the values, thus locating the base isotherm ACB.   Values on any other isotherm are then obtained from the relation

$$H_t = H_{t_0} + \int_{t_0}^{t} (C_p)_x \, dt \quad (IX.91)$$

where $(C_p)_x$ = specific heat (or molal heat capacity) of any solution.   In this way, for example, point D on Fig. IX.12 is located from C as a starting point.   Heat of solution data at other than the base isotherm would be useful as a check.

FIG. IX.12.—Construction of an enthalpy-concentration diagram for the case of two completely miscible liquids.

If the available data were (1) the specific heats of the two pure components and (2) heats of solution at several temperatures, the data of (1) would locate the termini of the several isotherms along the $x = 0$ and $x = 1$ axes and the intermediate points would then be located from the heat of solution data by Eq. (IX.51).   Other isotherms could be interpolated by plotting smooth curves at constant x on an Ht plane.

If the system were a salt and water and the available data consisted of (1) specific heats of water and several solutions as a function of temperature and (2) heats of dilution at one temperature t_0, the procedure would be somewhat different because points on the $x = 1$ axis cannot be located. In this case one can make use of Eq. (IX.68), locating the H_B values along the $x = 0$ axis as previously outlined and obtaining q_∞ from the heat of dilution data.

We shall now consider the case of two completely miscible substances when both the liquid and vapor regions are to be included on the diagram. In addition to data already considered, this diagram will require (1) latent heats of vaporization of both pure components, (2) specific heats of pure vapors, (3) boiling point as a function of composition, and (4) dew points of various mixtures. Either (3) or (4) may be dispensed with if data on heat of vaporization at constant x are available. As before, both H_A and H_B can be made equal to zero at some one temperature, which may be either in the subcooled liquid region or in that of superheated vapor; for the present illus-
tration, we shall choose the former. Isotherms in the liquid region up to t_A, the boiling point of pure more volatile component (see Fig. IX.13), are located by methods already reviewed. Above this temperature, A is no longer stable as a liquid at the given constant pressure; but since the effect of pressure on the enthalpy of a liquid can be considered negligible, the value of H_A can still be determined by using pressures higher than the vapor pressure. Of course, if the isotherms are located by specific-heat data rather than from heats of solution, values of H_A are not necessary. In either case, the saturated-liquid line is readily located by the points of intersection of the isotherms and the vertical lines for the compositions related to

Fig. IX. 13.—Enthalpy-concentration diagram for both liquid- and vapor-phase regions.

these temperatures by the boiling-point line on a tx diagram.

For example, point A on Fig. IX.13 is located by the intersection of the t_2 isotherm and the ordinate x, where t_2 and x are the coordinates of a point on the boiling-point line. Points B and C on the saturated-vapor line are located by adding the latent heats of vaporization of the pure components to the values of H at the two ends of the liquid line. Other points on the saturated-vapor line are located in a similar way if data on the latent heats of vaporization at constant composition are available. Usually, such data are not available, and other means must be used to locate this line. The heats of solution of gases and vapors at low pressures are small and can be assumed equal to zero without serious error. From Eq. (IX.51) it is evident that the Hx isotherms in the vapor region are linear if $q_s = 0$, and hence they are located purely by the data on the two pure components. Below t_B (boiling point
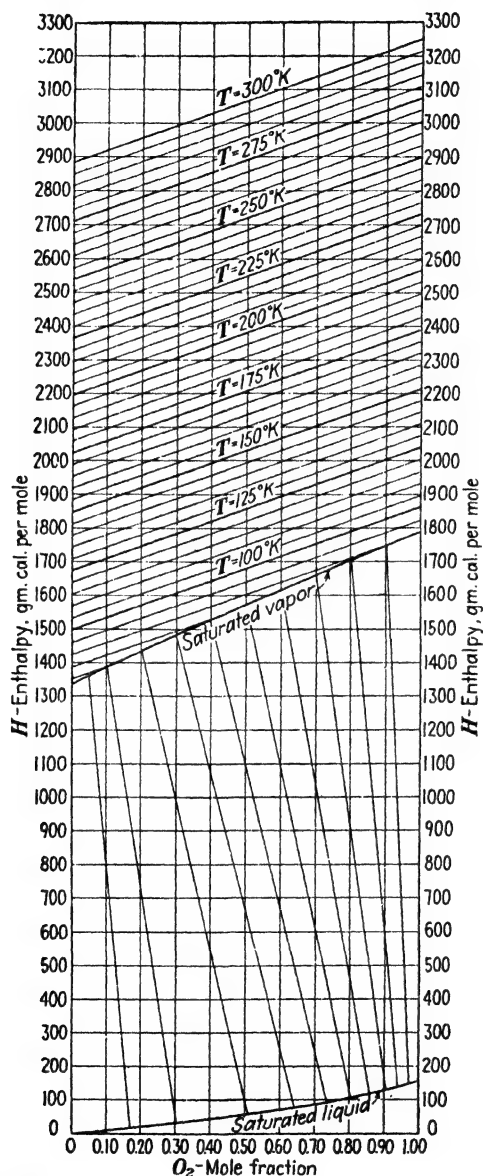
Fig. IX.14.—Enthalpy-concentration diagram for oxygen-nitrogen mixtures at 1 atm. abs. pressure. Basis: $H = 0$ for both liquid oxygen and liquid nitrogen at the normal boiling point of nitrogen. This is the same basis as that used in Millar and Sullivan, *Bur. Mines Tech. Paper* 424. (*This diagram is reproduced from one constructed by Dr. E. E. Lindsey, Jr., Chemical Engineering Department, Yale University.*)

of the less volatile component) the vapor phase is not stable for *B*-rich mixtures, but the isotherms can still be drawn by assuming lower pressures and that *H* is independent of pressure. The points on the saturated vapor line are readily located from the dew-point data. Thus if t_b and y are coordinates of a point on the dew line, the intersection of the t_b isotherm and the ordinate at y locates a point on the saturated-vapor line. An *Hx* diagram for mixtures of oxygen and nitrogen, covering the two-phase and superheated-vapor regions is given in Fig. IX.14. The lines running between the boundary curves for the two saturated phases are tie lines connecting the coexisting phases at equilibrium.

HEAT EFFECTS OF CHEMICAL PROCESSES

Definition of Heat of Reaction.—All chemical reactions are accompanied by energy changes as a result of the action of the forces involved in chemical bonding. If a reaction occurs adiabatically, the energy change due to the reaction may result either in an increase or in a decrease in the temperature of the system, depending on whether the net result is a decrease or an increase in the chemical energy. If the chemical energy of the system decreases, there must be a corresponding gain in some other form of energy; this means that the kinetic energy of the molecules and/or their potential energy due to position must increase. If the reacting system is not isolated from the surroundings, some of the energy may be manifested as a transfer of heat either to or from the surroundings. For the special case where the final reacting system is brought to the same temperature as the initial system, the heat effect accompanying this change is known as the "heat of reaction." In order to give it quantitative meaning, one must specify the exact initial and final states of all the substances involved and state whether the change occurred at constant volume or constant pressure. In our discussion we shall restrict the treatment to reactions occurring at constant pressure since they are of the most importance in industry. The relation between them, already treated in Chap. III, is important since many heats of reaction are actually determined at constant volume. It is obvious that any heat of a reaction at constant pressure represents a difference in enthalpies between two states of the system. We may therefore define a heat of reaction as an isothermal difference of enthalpy between reaction products and initial reactants all in some definite standard state that might be characterized by the state of aggregation, the pressure, and sometimes the concentration in a solution. Heats of reaction are commonly given specific names depending on the type of reaction, for example, heat of formation, of combustion, of dissociation, of hydration, or of isomerization. Heats of formation, which are simply heat effects in any reaction between elements to form a compound are of

particular importance because from them the heat for any type of reaction may be derived merely by addition and subtraction.

We shall now illustrate these statements by specific examples.   Consider the reaction

$$SO_2 + \tfrac{1}{2}O_2 = SO_3$$

carried out by the steps indicated diagrammatically in Fig. IX.15. Assume that N_1 moles of SO_2 are continuously mixed isothermally at the constant pressure of 1 atm. with N_2 moles of oxygen.   Any isothermal mixing process has a heat effect, even though it may, as in this case (Q_1), be very small.   The mixture then flows to the reaction vessel where reaction is initiated by some means that need not be specified and the heat Q_2 is evolved (or absorbed, as the case may be), resulting
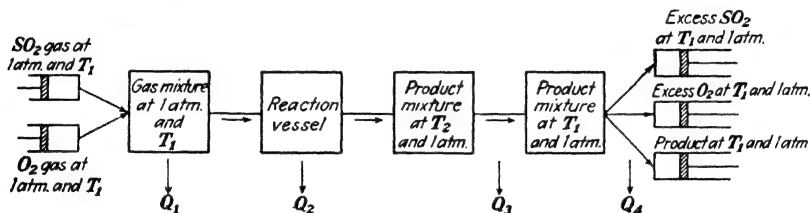
Fig. IX.15.—Steps in a simple chemical reaction.

in a product mixture at T_2.   This mixture is then brought to the initial temperature T_1, and the heat effect Q_3 results.   Assume that N_3 moles of SO_2 have reacted and that the product mixture is then separated isothermally into N_3 moles of SO_3 and the $N_1 - N_3$ moles of SO_2 and $(N_2 - \tfrac{1}{2}N_3)$ of oxygen that remain unreacted, the accompanying heat effect being Q_4.   Assume all the SO_3 to be finally obtained in the solid form, which would be the equilibrium state for this condition.   An energy balance on the over-all process yields

$$N_1H_1 + N_2H_2 = Q_1 + Q_2 + Q_3 + Q_4 + (N_1 - N_3)H_1$$
$$+ (N_2 - \tfrac{1}{2}N_3)H_2 + N_3H_3$$

where H_1, H_2, and H_3 are the molal enthalpies of SO_2, O_2, and SO_3 (solid), respectively, at T_1 and 1 atm.

$$\begin{aligned} \text{Over-all } \Delta H &= (N_1 - N_3)H_1 + (N_2 - \tfrac{1}{2}N_3)H_2 + N_3H_3 - N_1H_1 - N_2H_2 \\ &= N_3(H_3 - H_1 - \tfrac{1}{2}H_2) \\ &= -(Q_1 + Q_2 + Q_3 + Q_4) \end{aligned}$$

The ΔH per mole of one of the reactants or products, for example, per mole of SO_2 or of SO_3, is

$$\frac{\text{Over-all } \Delta H}{N_3} = -\frac{Q_1 + Q_2 + Q_3 + Q_4}{N_3}$$

and this is the quantity called "heat of reaction." Since it is an enthalpy difference, it must be quite independent of the individual steps and their respective heat effects. Thus the temperature actually attained in the reaction vessel or the temperature T_2 of the product mixture is immaterial. It will depend, however, on the exact initial and final states of the three chemical individuals. For example, if the SO_3 were left in the gaseous state instead of the solid state, H_3 would be different and a different heat of reaction would result. In the particular case here illustrated the heats Q_1 and Q_4 would be quite negligible and could be disregarded in the actual experimental determination of the heat of reaction. The states of the reactants and products to which a given heat of reaction refers are commonly designated in the following manner:

$$H_2 \ (g, 1 \text{ atm.}) + \tfrac{1}{2}O_2 \ (g, 1 \text{ atm.}) = H_2O \ (l, 1 \text{ atm.})$$
$$\Delta H_{298} = -68,318 \text{ g.-cal./g.-mole}$$
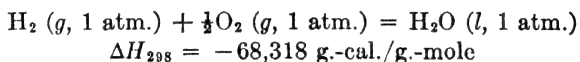
where g = gas and l = liquid.

ΔH_{298} means that the initial and final temperature states are 25°C. or 298°K. In this particular example it is obvious that the reactants would be taken as gases at 1 atm. (or near enough to 1 atm. so that any enthalpy change due to pressure is negligible)[1] and the designation of the states could be omitted, but this is not true of the product. Although liquid water is the only stable state at this temperature and pressure, at higher temperatures the stable state would be the gaseous one. Problems involving heats of reaction usually embrace a range of temperatures, and it is convenient to consider any given substance in one reference state. For example, one might be interested in the reaction

$$CO + H_2O = CO_2 + H_2$$
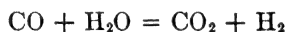
at 500°C. and 1 atm. where the water would be a gas. The heat of this reaction would commonly be obtained from heats of reaction referred to 25°C. and 1 atm. where water would exist as a liquid. Now it is permissible to consider a ΔH for this reaction at 25°C. with H_2O in the gaseous state and therefore at a pressure equal to or less than the vapor pressure because the ΔH due to any difference in pressure on the water vapor would be negligible.

In some cases it is desirable to choose one or more of the reference states as that of a solution rather than the pure substance. For example, the reaction

$$SO_3(g) + H_2O(l) = H_2SO_4(aq)$$
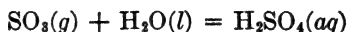
[1] In some cases, particularly when values of enthalpy or entropy are obtained from spectroscopic data, it may be desirable to take account of the difference between these quantities at zero pressure and at 1 atm. This can readily be done by the methods given in Chap. VI.

implies that the state of the product is that of a solution of H_2SO_4 in water so dilute that no further dilution would appreciably change the heat effect.

As discussed in Chap. I, the state of a solid is not always fixed when the state variables are fixed, and this has a bearing on heats of reaction involving solids. A classic example is that of carbon, which may exist in several different solid forms that, with the exception of the crystalline form, diamond, are incapable of exact definition. The heat of formation of CO_2 enters into the determination of the heat of formation of nearly every organic compound, and hence the heat of combustion of carbon is one of the most important of the fundamental thermochemical constants. In all modern thermochemical experimental work, graphite is used as the form of carbon, and we shall assume that this form of carbon is the standard one for all thermochemical equations.

Summation of Heats of Reaction.—The heat of any reaction is the algebraic summation of the heats of formation of all the compounds taking part in the reaction. For example, consider the reaction

$$aA + bB = lL + mM \tag{IX.92}$$

The heat of reaction ΔH_T per mole of A is given by

$$\Delta H_T = \frac{l}{a} \Delta H_L + \frac{m}{a} \Delta H_M - \frac{b}{a} \Delta H_B - \Delta H_A \tag{IX.93}$$

ΔH_A, ΔH_B, etc., are the heats of formation per mole of the respective substances. This follows, of course, from the nature of the property, H, and implies that all the ΔH's are referred to the same temperature and that all elements involved in the formation reactions are always taken in the same standard state. If one of the reacting constituents in Eq. (IX.92) is an element, its heat of formation is, of course, zero by definition. Since all heats of reaction are derivable in a simple manner from heats of formation, the best compilation of such data is a table of heats of formation at a standard temperature such as $25°C$. The enthalpies of all elements in a standard state at this temperature are taken to be zero. The heat of formation is, of course, the enthalpy of the compound in a particular standard state at this same temperature.

For a source of thermochemical data, the reader is particularly referred to the very extensive compilation by Bichowsky and Rossini,[1] which covers all inorganic substances for which data are available and organic compounds with one and two carbon atoms. A more recent compilation for 27 gaseous hydrocarbons was published by Rossini.[2]

[1] Bichowsky, F. R., and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936.

[2] Rossini, F. D., *Chem. Rev.*, **27**, 1–15 (1940).

Illustration 11.—Calculate the heat of the reaction

$$2H_2O(g) + CH_4 = CO_2 + 4H_2$$

at 25°C., given the following heats of formation, also at 25°C.:

$$\Delta H \text{ of formation of } CO_2 = -94,030 \text{ g.-cal./g.-mole}$$
$$\Delta H \text{ of formation of } H_2O(g) = -57,798 \text{ g.-cal./g.-mole}$$
$$\Delta H \text{ of formation of } CH_4 = -17,865 \text{ g.-cal./g.-mole}$$

ΔH for the reaction, per mole of CH_4, is

$$-94,030 + 4 \times 0 - (-2 \times 57,798) - (-17,865) = +39,430 \text{ g.-cal.}$$

This is a heat absorption; in other words, the reaction is an endothermic one.

Very few heats of reaction are directly determined from actual experimental measurements on the reaction itself. This would be very inconvenient and in the large majority of cases practically impossible. Again owing to the property H, most heats of reactions can be derived from others by a combination of the heats of reactions which are steps of the main reaction. For example, all heats of formation of organic compounds containing only carbon, hydrogen, and oxygen can be calculated from the heat of combustion of the compound (complete combustion to H_2O and CO_2 assumed) and the heat of combustion of carbon and of hydrogen. Thus the heat of the reaction

$$C + \tfrac{1}{2}O_2 + 2H_2 = CH_3OH(g) \qquad (\Delta H_1)$$

is obtained by an algebraic summation of the heats for the reactions

$$CH_3OH(l) + 1\tfrac{1}{2}O_2 = CO_2 + 2H_2O(l) \qquad (\Delta H_2)$$
$$CH_3OH(l) = CH_3OH(g) \qquad (\Delta H_3)$$
$$C + O_2 = CO_2 \qquad (\Delta H_4)$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O(l) \qquad (\Delta H_5)$$
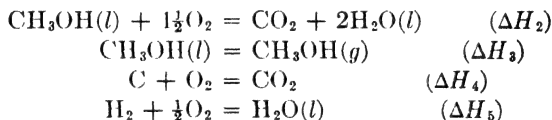
By combining the last four equations so as to give the first equation, one sees that

$$\Delta H_1 = \Delta H_3 - \Delta H_2 + \Delta H_4 + 2\Delta H_5$$

There is one difficulty with this procedure. Many heats of reaction are very small in magnitude compared with heats of combustion, and hence it is difficult to obtain a figure even of only fair accuracy without a highly elaborate and specialized technique. Thus the heat of combustion of n-hexane is about twenty-five times its heat of formation, and hence any error in the former is multiplied about twenty-five fold in the latter. An even more striking example is given by the following isomerization reaction:

$$n\text{-hexane} = 3\text{-methyl pentane}$$
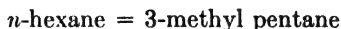
The heat of isomerization is only about 0.10 per cent of the heats of

combustion of either hexane. In spite of this, Rossini and coworkers[1] at the Bureau of Standards have developed techniques of very high accuracy permitting a determination of this heat of isomerization with an uncertainty of about ± 20 per cent. This is, of course, an extreme case chosen to emphasize the principle.

Heats of Reaction from Equilibrium Data.—Heats of reaction are also obtainable from equilibrium measurements by an application of the relation

$$\Delta H = RT^2 \left(\frac{\partial \ln K_a}{\partial T} \right)_p \qquad (IV.260)$$

If values of K_a are known as a function of temperature, the slope can be obtained either by algebraic or by graphical means. This method is quite accurate in the case of ionic equilibria where K_a is obtained from e.m.f. measurements but is only an approximation for reactions at elevated temperatures where accurate determination of K_a is the exception rather than the rule.

If ΔH is assumed to be independent of the temperature over short ranges, Eq. (IV.260) becomes

$$\Delta H = \frac{R \ln (K_{a_2}/K_{a_1})}{(1/T_1) - (1/T_2)} \qquad (IX.94)$$

and two values of K_a at two different temperatures (not too close together) suffice to determine ΔH. In this case, the ΔH is assumed to be the value at the arithmetic mean temperature.

If the equilibrium data can be represented by the relation

$$\log K_a = \frac{A}{T} + B$$

then

$$\frac{\partial \ln K_a}{\partial T} = - \frac{2.303A}{T^2}$$

and

$$\Delta H = -2.303AR \qquad (IX.95)$$

This method has been used in a number of instances but the accuracy of the result is always uncertain.

Illustration 12.—Using the data of **Fig. XI.2**, calculate the heat effect for the reaction

$$C_2H_4 + H_2O(g) = C_2H_5OH(g)$$
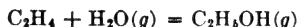
The experimental data are represented by the equation

$$\log K_p = \frac{2,132}{T} - 6.241$$

where T is in degrees Kelvin.

[1] An incomplete list of papers is as follows: KNOWLTON, J. W., and F. D. ROSSINI, *Bur. Standards J. Research*, **22**, 415 (1939). PROSEN, E. J. R., and F. D. ROSSINI, *Bur. Standards J. Research*, **27**, 289 (1941); 519 (1941).

Substituting in Eq. (IX.95),

$$\Delta H = -2.303 \times 2,132 \times 1.987 = -9,750 \text{ g.-cal./g.-mole}$$

at the mean temperature of 500°K.

This is not in very good agreement with the value obtained from the thermal data assembled by Parks,[1] *viz.*, −11,235.

Heat of Reaction and Structure.—A quantitative relationship of ΔH of reaction to structure would be a great boon in the estimation of heats of formation of organic compounds for which experimental data are not available. Although considerable attention has been devoted to this question, little of practical value has as yet been developed. If we consider a simple formation reaction such as

$$4C + 5H_2 = C_4H_{10}$$

we may regard the net result as being the formation of 3 carbon-carbon bonds and 10 carbon-hydrogen bonds. If a definite energy value could be assigned to each of these bonds, we should be able to calculate the energy of formation of this or any similar compound by a simple addition. Experiment shows that the actual situation is not so simple as this. The bond energies are not constants but depend on the configuration of the molecule. For example, if the simple additive relation for bond energies held, isomers of a given compound such as pentane should all have the same heat of formation, but experiment reveals a significant difference.

A small beginning has been made in finding some relationships in the case of homologous series that permit some predictions to be made. For example, Rossini[2] has shown that for the three homologous series, *n*-alkane hydrocarbons, *n*-alkene hydrocarbons, and primary *n*-alkyl alcohols, the following relation holds for the heat of formation:

$$\Delta H = A + Bn + \Delta \qquad (IX.96)$$

where A = a constant, characteristic of the end group of a series (H for normal paraffins and OH for alcohols).

B = universal constant for all three series.

n = number of carbon atoms.

Δ = deviation from linear relation (small after $n = 2$ and 0 for $n > 5$).

This relation can be used to predict values of ΔH of formation for those members of the series for which data are now lacking.

Effect of Temperature on Heat of Reaction.—All heats of chemical reaction given in the usual compilations are the standard heats for a

[1] PARKS, G. S., *Ind. Eng. Chem.*, **29**, 845 (1937).

[2] ROSSINI, F. D., *Ind. Eng. Chem.*, **29**, 1424 (1937).

temperature around room temperature—usually 25°C. for modern determinations. In a specific problem one may wish to use the heat for some other temperature, and this is readily obtained by calculation from specific-heat data. The method of calculation goes back to the fundamental relation

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

If we apply this to each chemical substance taking part in a reaction that is represented in general terms by Eq. (IX.92) and make an algebraic summation, we can write

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p \qquad (IX.97)$$

where ΔH = heat of reaction per mole of A

$$= \frac{m}{a} H_M + \frac{l}{a} H_L - \frac{b}{a} H_B - H_A$$

and $$\Delta C_p = \frac{m}{a}(C_p)_M + \frac{l}{a}(C_p)_L - \frac{b}{a}(C_p)_B - (C_p)_A$$

Each of the H's is a heat of formation for the substance in question.

The following qualitative deductions can be made on the basis of Eq. (IX.97). If the total heat capacity of the reaction products is greater than that of the reactants, the exothermic heat of reaction will decrease as the temperature increases, and vice versa. In other words, if the reaction is exothermic (ΔH is negative), the numerical value of ΔH will decrease with the temperature; but if it is endothermic and the products have the greater heat capacity, ΔH (positive) will increase with the temperature. If the products and reactants have the same total heat capacity, the heat of reaction will be independent of temperature.

Integrating Eq. (IX.97),

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^{T} \Delta C_p \, dT \qquad (IX.98)$$

From this equation, ΔH_T, at any temperature is readily obtained from ΔH_{T_0}, the value at a base temperature, if C_p for each substance is known as a function of temperature over the range in question. If the molal heat capacity of each substance is represented by an equation like Eq. (IX.15), Eq. (IX.98) can be developed to

$$\Delta H_T = \Delta H_{T_0} + \Delta\alpha(T - T_0) + \tfrac{1}{2}\Delta\beta(T^2 - T_0^2) + \tfrac{1}{3}\Delta\gamma(T^3 - T_0^3) \quad (IX.99)$$

where $$\Delta\alpha = \frac{m}{a}\alpha_M + \frac{l}{a}\alpha_L - \frac{b}{a}\alpha_\beta - \alpha_A \qquad (IX.100)$$

with similar expressions for $\Delta\beta$ and $\Delta\gamma$.

Equation (IX.97) is frequently integrated without limits, giving

$$\Delta H = \Delta H_0 + \Delta \alpha T + \tfrac{1}{2} \Delta \beta T^2 + \tfrac{1}{3} \Delta \gamma T^3 \qquad (IX.101)$$

where ΔH_0 is a constant of integration and is not equal to the heat of reaction at any given temperature.

Effect of Pressure on Heat of Reaction.—This is of far less importance than the effect of temperature and can be covered sufficiently in one paragraph. It is of some importance in connection with high-pressure gas reactions where the effect of pressure is appreciable. From Eq. (III.96),

$$\left(\frac{\partial H}{\partial p} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_p$$

Proceeding as in the case of temperature, we have

$$\left(\frac{\partial \Delta H}{\partial p} \right)_T = \Delta v - T \left(\frac{\partial \Delta v}{\partial T} \right)_p$$

or

$$\Delta H = \Delta H^\circ + \int_{p^\circ}^{p} \Delta v \, dp - T \int_{p^\circ}^{p} \left(\frac{\partial \Delta v}{\partial T} \right)_p dp$$

where

$$\Delta v = v_L + v_M - v_A - v_B$$

when the standard state of each substance is the pure component at p°.

To calculate ΔH at the elevated pressure one needs an equation of state or the equivalent data for each substance taking part in the reaction.

General Heat Effect of a Reaction.—Up to this point we have been concerned mainly with a particular heat effect known as the heat of reaction. It is now desirable to generalize the equations a little to include any heat effect of a reaction. Even the equations for heat of reaction [for example, Eqs. (IX.97) to (IX.101)] are limited to the case in which no latent heat changes are involved since Eq. (IX.97) implies only sensible-heat changes. A more general equation for the heat effect should provide for latent heats, for ratios of reactants other than the stoichiometric, for the presence of inerts, for incomplete reaction, and for all heat effects between the two limiting cases of isothermal and adiabatic reaction. To obtain such an equation, consider the cycle of changes represented in Fig. IX.16. The term "reactants" is understood to mean all substances entering the reaction chamber or present in it at some initial time whether they all take part in the reaction or not. The term "products" includes all substances leaving the chamber or present in it when the reaction is considered to be concluded. For the cycle,

$$-Q_1 + Q + Q_2 - Q_3 = 0 \qquad (IX.102)$$

Now each of the Q's for the steps involving a temperature change consists, in general, of a summation of sensible- and latent-heat terms.

For example, for a component A we should have

$$Q = N_A \, \Delta H_A = N_A \int_{T_0}^T C_{p_A} \, dT + N_A L_0 \qquad \text{(IX.103)}$$

The integral represents the total sensible-heat change for component A between the base temperature T_0 and the general temperature T. L_0 is the latent heat of phase change of the component, if any such change occurs between the temperatures considered, at the base temperature T_0. Actually, of course, any vaporization or condensation that occurs in a reaction mixture will take place over a range of temperatures and practically none of it at the base temperature. However, we are justified in considering all the vaporization or condensation as taking place at the base temperature because ΔH is independent of the actual path and hence we are at liberty to choose the simplest and most convenient path since all are equivalent. By referring all latent heats to the base or
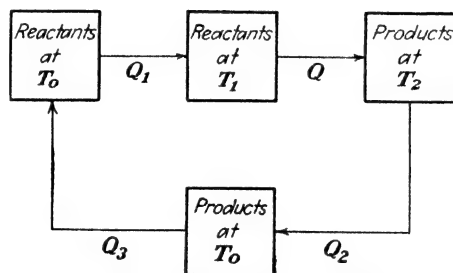
Fig. IX.16.—Cyclic reaction process.

standard temperature (usually 25°C.) we avoid having to deal with the specific heats of more than one phase of a given component. Furthermore, it does not matter if the path we have chosen to evaluate ΔH is not strictly at constant pressure provided that all pressures are sufficiently low so that the usual assumption of ideal gas can be made, which then implies that ΔH is independent of pressure.

Consequently, we can express Q_1 and Q_2 in Eq. (IX.102) as a summation of a series of equations like (IX.103) for reactants and for products. $-Q_3$ is the total heat effect for the reverse reaction at the base temperature or ΔH_{T_0}, the heat of reaction at T_0, multiplied by the number of moles of the reactant (assumed component A) on which the heat of reaction is based and by ζ, the fraction that reacts. We may therefore develop Eq. (IX.102) to the following form:

$$-\Sigma_R N_i \left(\int_{T_0}^{T_1} C_p \, dT + L_0 \right) + \Sigma_P N_i \left(\int_{T_0}^{T_1} C_p \, dT + L_0 \right) + \zeta N_A \, \Delta H_{T_0}$$
$$+ Q = 0 \quad \text{(IX.104)}$$

Σ_R signifies a summation for all the reactants and Σ_P the same for all

the products, each of the terms $\int C_p \, dT + L_0$ being multiplied by the number of moles of the given component. This includes all inerts that will appear both in the reactants and products, and the latter also includes all excess of reactants.

For convenience in later application, we shall write this equation in the following abbreviated form:

$$\Sigma_P H - \Sigma_R H + \zeta N_A \Delta H_{T_0} + Q = 0 \qquad (IX.105)$$

The most important case in which latent heats must be taken into account is that of the combustion of fuels containing hydrogen. The necessity for taking account of the latent heat of condensation of the water vapor in making the summation for the products can be avoided by leaving the equivalent term out of $N_A \Delta H_{T_0}$. In other words, one can omit the latent-heat quantity for water from the heat of combustion, giving a quantity that is called the "net heating value" of the fuel. If Eq. (IX.15) is chosen to represent the heat-capacity data, Eq. (IX.104) may be integrated to give

$$-\Sigma_R N_i[\alpha(T_1 - T_0) + \tfrac{1}{2}\beta(T_1^2 - T_0^2) + \tfrac{1}{3}\gamma(T_1^3 - T_0^3)] - \Sigma_R N_i L_0$$
$$+ \Sigma_P N_i[\alpha(T_2 - T_0) + \tfrac{1}{2}\beta(T_2^2 - T_0^2) + \tfrac{1}{3}\gamma(T_2^3 - T_0^3)] + \Sigma_P N_i L_0$$
$$+ \zeta N_A \Delta H_{T_0} + Q = 0 \qquad (IX.106)$$

$\Sigma_R N_i \alpha$, $\Sigma_R N_i \beta$, and $\Sigma_R N_i \gamma$ are the summations of the constants α, β, and γ of the C_p equations for all the reactants multiplied by the respective number of moles. $\Sigma_P N_i \alpha$, etc., are the same for all the products. To make this clearer we shall develop two of these expressions as follows:

$$\Sigma_R N_i \alpha = N_A \alpha_A + N_B \alpha_B + N_I \alpha_I$$
$$\Sigma_P N_i \beta = N_L \beta_L + N_M \beta_M + N_I \beta_I$$

where I refers to inert components.

Equation (IX.106) is useful for calculating T_2, the temperature attained in a reaction, given the initial temperature of the reactants, T_1, the heat of reaction at the base temperature, T_0, the heat given off to the surroundings, and the specific heats of the various constituents. When $T_1 = T_2 = T$ and $\zeta = 1$, $Q = -N_A \Delta H_T$ and Eq. (IX.106) becomes substantially the same as Eq. (IX.99) except for its more general form.

Illustration 13.—Calculate the heat of the reaction

$$CH_4 + 2H_2O(g) = CO_2 + 4H_2$$
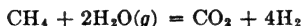
at 500°C.

From Illustration 11, $\Delta H_{T_0} = 39{,}430$ g.-cal. per g.-mole of CH_4. From Table IX.1,

$$\Delta\alpha = 6.85 + 4(6.88) - 2(6.89) - 3.38 = 17.21$$
$$\Delta\beta = [8.533 + 4(0.066) - 2(3.283) - 17.905] \times 10^{-3} = -15.674 \times 10^{-3}$$
$$\Delta\gamma = [-24.75 + 4(2.79) - 2(3.43) + 41.88] \times 10^{-7} = 21.43 \times 10^{-7}$$

Substituting in Eq. (IX.99),

$$\Delta H_T = 39,430 + 17\,21(773 - 298) - \frac{15.674}{2} \times 10^{-3}[(773)^2 - (298)^2] + \frac{21.43}{3}$$
$$\times 10^{-7}[(773)^3 - (298)^3] = 43,950$$

Illustration 14.—A gas mixture consisting of 94 per cent hydrogen, 3 per cent nitrogen, and 3 per cent carbon monoxide is to be freed of the latter gas by passing the mixture through a suitable catalyst bed to bring about the reaction

$$CO + 3H_2 = CH_4 + H_2O(g)$$
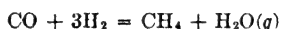
Assume that the gas enters the catalyst bed at 500°C. and 1 atm., that this reaction is complete without side reactions, and that no heat is transferred to or from the surroundings. Estimate the temperature of the gases leaving the catalyst bed.

The ΔH of formation of CO at 25°C. $= -26,394$. Using the other heats of formation from Illustration 11,

$$\Delta H_{T_0} = -57,798 - 17,865 + 26,394 = -49,270 \text{ c.h.u./lb.-mole CO}$$

The amounts of reactants and products per mole of carbon monoxide are as follows:

Gas	Reactants	Products
CO	1	0
H_2	31.3	28.3
N_2	1	1
CH_4	0	1
H_2O	0	1

The solution is to be made using Eq. (IX.104) with T_2 as the unknown. $T_0 = 298°K.$, and $T_1 = 773°K.$ Instead of evaluating the integrals by means of the C_p equations, this time we shall use the mean C_p table of Justi and Lüder (Table IX.2) and the following mean C_p data for CH_4 also given by Justi and Lüder:

$t°C$	C_p, g.-cal. per g.-mole	$t°C.$	C_p, g.-cal. per g.-mole
0	8.24	600	12.03
100	8 66	700	12.62
200	9 40	800	13.17
300	10.10	900	13.68
400	10 77	1000	14.17
500	11 41		

Using Eq. (IX.23), the first term of Eq. (IX.104) is evaluated as follows:

$$\Sigma_R N_i \int_{T_0}^{T_1} C_p\, dT = 7.19(500) - 6.97(25) + 31.3[6.99(500) - 6.92(25)]$$
$$+ 7.15(500) - 6.97(25) = 110,800$$

The second term of Eq. (IX.104) must be evaluated by trial.

Assume $t_2 = 700°C$. Reading mean C_p from the table,

$$\Sigma_P N_i \int_{T_2}^{T_0} C_p \, dT = 28.3[7.03(700) - 6.92(25)] + 7.27(700) - 6.97(25)$$
$$+ 12.62(700) - 8.34(25) + 8.74(700) - 8.03(25) = 153{,}570$$

Substituting in Eq. (IX.104),

$$-110{,}800 + 153{,}570 - 49{,}270 + 0 \neq 0$$

or
$$-160{,}070 + 153{,}570 \neq 0$$

It is evident that the assumed temperature is too low. A few more trials show that the correct value is about $t = 727°C$.

Illustration 15.—Calculate the maximum flame temperature for the burning of methane with 20 per cent excess air if both air and methane are preheated to $300°C$.

The maximum flame temperature of a combustion reaction is assumed to be the temperature that would be attained if the reaction were adiabatic. Actual flame temperatures are somewhat less, but the difference is small enough so that the calculated values are sufficiently good for most engineering purposes.[1]

The reaction may be written

$$CH_4 + 2.40 \, O_2 + \tfrac{79}{21} \times 2.40 N_2 = CO_2 + 2H_2O(g) + 0.40 \, O_2 + \tfrac{79}{21} \times 2.40 N_2$$
$$\Delta H_{T_0} = -212{,}790 \text{ g.-cal./g.-mole } CH_4 \quad \text{(total heating value)}$$
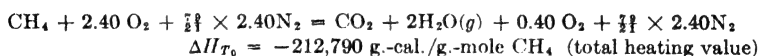
This assumes complete combustion and no other reactions occurring. The specific heat data of Table IX.1 will be used in the evaluation of Eq. (IX.106).

$\Sigma_R N_i \alpha = 9.03(6.30) + 2.40(6.26) + 3.38 = 75.30$
$\Sigma_R N_i \beta = [9.03(1.819) + 2.40(2.746) + 17.91] \times 10^{-3} = 0.04094$
$\Sigma_R N_i \gamma = [9.03(-3.45) + 2.40(-7.70) - 41.88] \times 10^{-7} = -0.915 \times 10^{-5}$
$\Sigma_P N_i \alpha = 9.03(6.30) + 0.40(6.26) + 2(6.89) + 6.85 = 80.13$
$\Sigma_P N_i \beta = [9.03(1.819) + 0.40(2.746) + 2(3.283) + 8.533] \times 10^{-3} = 0.0326$
$\Sigma_P N_i \gamma = [9.03(-3.45) + 0.40(-7.70) + 2(3.43) - 24.75] \times 10^{-7} = -0.522 \times 10^{-5}$

Again a trial value of t_2 must be assumed.

Let $t_2 = 2000°C$.

Substituting in Eq. (IX.106),

$$-25{,}130 + 241{,}900 - 212{,}790 - 0 \neq 0$$

It is evident that the assumed temperature is a little too high.

Let $t = 1950°C$.; then $-237{,}900 + 235{,}300 \neq 0$. It is evident that the correct value lies between these two, and $1970°C$. is obtained by a rough interpolation. This is sufficiently close to the correct solution. There is no point in splitting hairs in such a calculation since it is inherently not very precise anyway. The specific heats are not very accurately known at the high temperatures, and some dissociation of CO_2 and water vapor would take place at such a temperature. For example, at $2200°K$. ($1927°C$.) and a total pressure of 1 atm., water vapor is about 1.5 per cent dissociated into H_2 and O_2 and CO_2 about 5 per cent into CO and O_2. In an actual flue gas from

[1] JONES, LEWIS, FRIAUF, and PERROTT [*J. Am. Chem. Soc.*, **53**, 869 (1931)] measured the flame temperatures of various hydrocarbon gases burning in air by the spectral-line reversal method and compared them with the calculated values. The observed temperatures were 50 to $100°C$. lower. The difference is probably accounted for largely by radiation from the flame.

combustion the degree of dissociation would be considerably greater owing to the lower partial pressure of these gases. The dissociation of these gases can be allowed for in the calculation by methods that will be taken up in Chap. XI.

It is of interest to note that the theoretical flame temperatures for the burning of gases in air with no excess do not vary much with different gases in spite of very great differences in heat of combustion. For example, H_2 with a heating value of 319 B.t.u. per cu. ft. at 60°F. and 1 atm. has a theoretical flame temperature of about 2200°C., whereas benzene with a heating value more than ten times as great, or 3,675 B.t.u. per cu. ft., gives a temperature of 2240°C. This is, of course, due to the fact that the gases with the higher heating values also require correspondingly larger amounts of air for combustion. Most calculated flame temperatures for complete combustion in air with no excess and no preheating of the air or gas lie between 2000 and 2400°C. The temperature can be increased by preheating and/or by using oxygen or air enriched in it instead of ordinary air. The latter possibility is an interesting one that may be the basis for important future developments in high-temperature technology.

CHAPTER X

REFRIGERATION

Although refrigeration is usually regarded as the province of the mechanical engineer, there are so many ways in which low temperatures can be usefully applied in the chemical industries that it is important for the chemical engineer to be familiar with the general principles and to know the limitations and advantages of refrigerating processes and equipment in order to make an intelligent decision when confronted with a problem which involves the use of temperatures below that of the surroundings.

A brief and incomplete survey of the applications of refrigeration in the process industries would include such items as liquefaction of chlorine; production of solid CO_2; solvent recovery; gasoline from natural gas; condensation of volatile liquids like CS_2, ethyl ether, and CCl_4; crystallization of salts from solution; dehydration of gases and removal of impurities from them; air conditioning in the manufacture of rayon, photographic film, gelatin, and candy; separation of paraffin wax from petroleum; control of reaction rate in organic reactions such as nitration and diazotization; production of oxygen and nitrogen from air and hydrogen from coke-oven and other gases; and the liquefaction and storage of natural gas.

Methods of Producing Refrigeration.—In a broad sense, refrigeration is the science and art of producing and maintaining temperatures below that of the surrounding atmosphere. Low temperatures can be obtained in various ways, as follows: (1) allowing a phase change to take place in such a way as to extract heat, for example, the evaporation of a liquid such as water or ammonia or the melting of ice or the solution of a salt; (2) expanding a compressed gas or vapor so that it does external work; (3) expanding a gas in the Joule-Thomson way; (4) desorption of a gas; (5) demagnetization of a solid; (6) passage of an electric current through a bimetallic junction (Peltier effect). In fact, any reversible change involving the expenditure of work can be utilized to absorb heat and produce low temperatures. Method 1 is that most commonly used for commercial refrigeration. It is also the basis for the use of the large number of cooling mixtures, of which salt and ice is one of the commonest, that are useful for intermittent cooling on a small scale. Methods 2 and 3 are used for reaching very low temperatures on an industrial scale.

Methods 4 and 5 have been used for the production of very low temperatures in the labo:atory; 5, in particular, has been applied to the production of extremely low temperatures approaching absolute zero.   Method 6 is mentioned merely as a possible method that has never been applied in practice.   Any one of these processes can be considered as occurring (1) in an adiabatic system, in which case the temperature of the system itself will fall; (2) isothermally, with an accompanying influx of heat from the surroundings; or (3) by a combination of both these limiting conditions.

The continuous production of cold by purely mechanical means, such as the use of compression in a cycle involving alternate condensation of a vapor to a liquid and revaporization, is generally known as "mechanical refrigeration."   This is by far the most important method of maintaining low temperatures and will form the main subject matter of this chapter.   Methods of producing temperatures just a little under that of the atmosphere by allowing water to evaporate without any mechanical aid from a pump is very important for air conditioning and water cooling but will be considered outside the scope of this chapter. Methods for the production of very low temperatures (say less than $-100°F.$) are somewhat special and will be discussed briefly in this chapter.

The Ideal Refrigeration Cycle.—The maintenance of any temperature below that of the surroundings requires the continuous abstraction of heat at this temperature level and its rejection at some higher level. Thus refrigeration is essentially an operation involving the pumping of heat from one temperature level to a higher one.   This simple concept is of the greatest value in enabling one to visualize the essential elements of any process of refrigeration.   In discussing the second law of thermodynamics in Chap. II, it was shown that any reversible heat engine can be regarded also as a heat pump.   An engine operating on the Carnot cycle taking in heat at absolute temperature T_1 and rejecting it at T_2 was shown to have the maximum efficiency that could be attained by any heat engine operating between the given temperature limits.   The efficiency, which is the ratio of work done to heat absorbed at T_1, is given by[1]

$$\frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} \qquad (X.1)$$

For the basis of this equation, reference should be made to Chaps. II and III.   Since we are considering a completely reversible cycle, the Carnot engine may be imagined to operate in the reverse direction, taking in heat at T_2 and rejecting the amount Q_1 at T_1.   The same equation

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[1] For the sake of simplification, the mechanical equivalent of heat J is omitted from the equations in this chapter.

still applies; but since in heat pumping we are interested in knowing how much heat can be removed at the lower temperature with the expenditure of a given amount of work, Eq. (X.1) is generally put in the form[1]

$$\frac{W}{Q_2} = \frac{T_1 - T_2}{T_2} \tag{X.2}$$

Here T_2 refers to a heat reservoir or refrigerator at a temperature below that of the surroundings and T_1 to a heat reservoir or heat receiver at a temperature equal to or greater than that of the lowest temperature of any large mass in the surroundings (for example, the atmosphere or any large body of water). Hereafter, we shall generally use the symbol T_0 for this temperature. Equation (X.2) follows at once from Eq. (X.1) when use is made of the fact that

$$W = Q_1 - Q_2 \tag{X.3}$$

which follows from the first law.

Q_2/W, which is a measure of the refrigerating effect per unit of work done, is known as the "coefficient of performance" β. Equation (X.2) establishes the optimum performance that can be expected of any refrigerating machine operating between given temperature limits. No machine can be devised that will pump heat with a less expenditure of work. Furthermore, Eq. (X.2) implies that all reversible refrigerating machines operating between given temperature limits will have the same coefficient of performance irrespective of fluid used or of mechanism. In other words, the coefficient depends only on the temperatures. These statements are, in essence, nothing but statements of the second law of thermodynamics.

Let it be emphasized at this point that Eq. (X.2) is merely an expression which shows the very best that can be done by any refrigerating process. Owing to the inevitable irreversible effects in any practical process, it will require more work for a given amount of heat than is called for by the equation. The equation is useful in establishing an absolute standard of comparison and facilitating the analysis of an actual process. Comparison of the actual with the ideal points the way to possible improvements. The equation is also useful for rough estimates of the amount of work required to produce a given refrigeration. It also points to the following important facts:

1. Work per unit of refrigeration cannot be greatly affected by changing the working fluid. In the ideal cycle it is independent of the fluid, but in the actual cycle there will be differences between fluids, though, in the main, not great ones.

[1] The convention that work done on a system is negative will be adhered to only in those cases where algebraic addition of several work terms requires a sign convention.

2. Work will be increased as the temperature of the refrigerator is lowered.

3. Work will be increased as the temperature of the heat receiver increases.

Illustration 1.—One thousand B.t.u. per minute is to be continuously removed from a fluid mixture, which is thus maintained at a constant temperature of 10°F. The lowest temperature of any large mass in the surroundings is 60°F. What is the least amount of power, expressed as horsepower, that is necessary to accomplish this?

The heat removed at T_2 must be brought to at least 60°F. before it can be transferred out of the system to the surroundings. Therefore, $T_1 = 460 + 60 = 520°R$.

$$\text{Power (B.t.u./min.)} = 1,000 \times \frac{60 - 10}{470} = 106.4$$

$$\text{Hp.} = 106.4 \times \frac{60}{2,545} = 2.48$$

Equation (X.2) assumes a constant temperature T_2 at the refrigerator and also T_0, the temperature at the point of heat rejection. For the case where T_0 is constant but the temperature of the refrigerator is a variable temperature T, the equation takes the more general form

$$W = \int_{T_1}^{T_2} \frac{T_0 - T}{T} \, dQ \tag{X.4}$$

where T_1 and T_2 are the limits between which T varies. Since $dQ = dH$ for a substance cooling at constant pressure, Eq. (X.4) can also be written

$$W = \int_{T_1}^{T_2} \frac{T_0 - T}{T} \, dH \tag{X.5}$$

Illustration 2.—What is the least amount of work, expressed in kilowatt-hours, necessary to cool 1 lb.-mole of CO_2 at 1 atm. from 70 to −100°F. if a large supply of cooling water is available at 70°F.?

Assume
$$C_p = a + bT$$

where $a = 5.89$ and $b = 0.00563$ when T is in degrees Rankine and C_p is in B.t.u. per pound-mole.

By Eq. (X.5), since $dH = C_p \, dT$,

$$W = \int_{T_1}^{T_2} (a + bT) \frac{T_0 - T}{T} \, dT = {}_{T_1}^{T_2}\left[aT_0 \ln T - (a - bT_0)T - \frac{1}{2} bT^2 \right]$$

Substituting limits and noting that $T_1 = T_0$,

$$W = aT_0 \ln \frac{T_0}{T_2} - (a - bT_0)(T_0 - T_2) - \frac{1}{2} b(T_0^2 - T_2^2)$$

$$T_0 = 530°R.$$
$$T_2 = 360°R.$$
$$W \text{ (B.t.u.)} = 286$$
$$= 0.084 \text{ kw.-hr.}$$

The simple Carnot refrigeration cycle to which Eq. (X.2) applies may be represented on a temperature-entropy diagram as shown in Fig. X.1. AB represents the isothermal heat absorption, BC the adiabatic compression of the working fluid, CD the isothermal rejection of heat, and DA adiabatic expansion to return the fluid to the initial state at A.

From the two laws of thermodynamics,

$$Q_2 = T_2(S_B - S_A) \qquad \text{(X.6)}$$

$$Q_1 = T_0(S_C - S_D) = T_0(S_B - S_A) \qquad \text{(X.7)}$$

$$-W = Q_1 - Q_2 = (T_0 - T_2)(S_B - S_A) \qquad \text{(X.8)}$$

From these equations one sees that the area under line AB down to the $T = 0$ axis represents Q_2. Similarly, the area under DC equals Q_1, and the enclosed area gives the work.
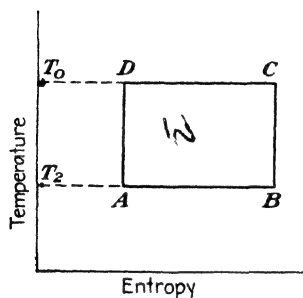
FIG. X.1.—Simple Carnot refrigeration cycle.
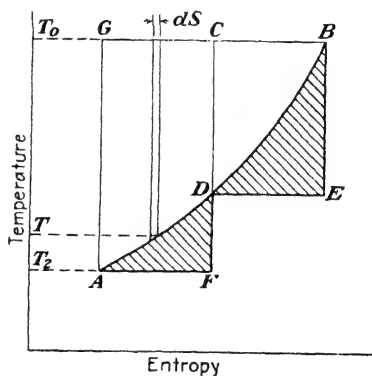
FIG. X.2.—Minimum work to cool a fluid.

To cool a substance from T_0 to T_2 according to path BA, in Fig. X.2, heat must be removed at various temperature levels. Let us first assume that this is done by two refrigerating machines operating on the Carnot cycles $BCDE$ and $CGAF$. It is evident that there will be irreversible transfers of heat since the working fluids, at all but two points, will be lower in temperature than the substance giving up the heat. This will result in the expenditure of an amount of work given by the areas of these two rectangles. By utilizing a larger number of machines, each of smaller capacity, it is evident that the enclosed area can be reduced. By proceeding to the limit and taking cycles of infinitesimal capacity (dS change in entropy) one arrives at a reversible process with the minimum work. The cross-hatched areas show the reduction in work over the first case using only two Carnot refrigerators. From the

diagram it is evident that the work for the case of an infinite number of Carnot heat pumps is given by

$$W = \int_{T_2}^{T_0} (T_0 - T) \, dS \tag{X.9}$$

and since

$$dS = \frac{dH}{T} \tag{X.10}$$

Eq. (X.9) is identical with Eq. (X.5). Equation (X.5) may also be put in the form

$$W = T_0 \, \Delta S - \Delta H \tag{X.11}$$

where the Δ's are between the limits of T_2 and T_0. Note that the right-hand side of Eq. (X.11) is the availability function defined in Chap. III. Thus we have the simple rule that, for any change of state of a substance involving the removal of heat, the minimum work required is equal to the availability.

Use of Heat to Produce Cold.—It should not be inferred from the preceding discussion that work must necessarily be done to accomplish a refrigerating effect in a continuous manner. It is true that the most important process of mechanical refrigeration is the compression process in which the heat absorbed at the refrigerator causes the vaporization of a liquid and the vapor is then compressed and cooled to condense it and complete the cycle. Obviously, work is required in this process to compress the vapor; and if we go back to the ultimate source of this work, we find that it would normally be obtained from a heat engine. Thus we may regard the compression-refrigeration process as the combination of a heat engine and a heat pump, the one supplying work that is directly used in the other. The net result is that a certain quantity of heat at some temperature above that of the surroundings is utilized to pump heat from a temperature level below that of the surroundings. It is a logical step to assume that the heat might be directly applied to produce the heat-pumping effect without the intermediate step of being transformed into external work. This is exactly what happens in the absorption process of refrigeration, which will be described later.

From the ideas just presented and Eqs. (X.1) and (X.2) it is easy to derive

$$\frac{Q_2}{Q_1} = \frac{T_2(T_1 - T_0)}{T_1(T_0 - T_2)} \tag{X.12}$$

Subscripts 1, 2, and 0 refer, respectively, to the heat source, the refrigerator, and the heat absorber. Q_2/Q_1 might be regarded as the coefficient of performance of a refrigerating cycle in which heat rather than work is directly utilized to produce the cooling effect.

Refrigerating Capacity.—It is convenient to have a unit of refrigerating capacity so that a refrigerating machine can be given a size rating, just as one rates a boiler by its boiler horsepower or a steam engine by its horsepower. The unit of refrigeration capacity is the ton of refrigeration per 24 hr., generally abbreviated to "ton." It is arbitrarily defined so that it equals the removal of 200 B.t.u. per min.[1] without regard to the conditions under which it is removed. The capacity of any actual refrigerating unit will vary greatly with the operating conditions, and for this reason it is necessary to define the major variables so that the ton rating will be standardized. The power required for refrigeration is frequently stated in horsepower or kilowatts per ton. Thus the horsepower per ton refrigeration for the case of Illustration 1 is $2.48/5 = 0.496$. Obviously, the power per ton will vary greatly with the conditions.

COMPRESSION REFRIGERATION

Actual Refrigeration Cycles.—In treating the Carnot, or ideal, refrigeration cycle it was not necessary to consider any details concerning the mechanism of the process. In fact, the great advantage of this method of analysis is its great simplicity, which is due to the fact that it is independent of mechanism. No actual refrigeration process can equal the Carnot ideal one. It is our next task to treat actual cycles and show how and to what extent they depart from the ideal. Those actual cycles in which the work of a compressor is utilized to produce a refrigerating effect may be said to differ from the ideal Carnot cycle in two general ways. In the first place, the cycle itself, even if the mechanism for realizing it were perfect, has certain inherent irreversible effects that make it less efficient than the Carnot cycle. In the second place, there are the inevitable irreversible effects such as friction, imperfect heat insulation, and necessary temperature differences to cause heat transfer that are removable at the limit but that are present to greater or less degree in any practical process.

Gas-expansion Process.—This process, shown diagrammatically in Fig. X.3, uses as working fluid a gas such as air that is not condensed to a liquid at any point in the process. The gas enters a compressor, where it is raised to a higher pressure and at the same time to an elevated temperature as a result of adiabatic compression. The compressed gas is cooled at constant pressure substantially to the temperature of the cooling water and is then expanded in an engine cylinder to a pressure which in the ideal case would be equal to that at the compressor

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[1] The historical basis for the unit is the fact that the melting of 1 ton of water ice at 32°F. to form water at 32°F. requires the extraction of the latent heat of 288,000 B.t.u. This amount of heat per 24 hr. is equivalent to 200 B.t.u. per min.

intake.   The expander is generally connected to the drive shaft of the compressor so that the work done by the expanding gas is directly utilized in the compression, the motor supplying only the difference.   The cold gas resulting from the expansion is led through a refrigerator, where
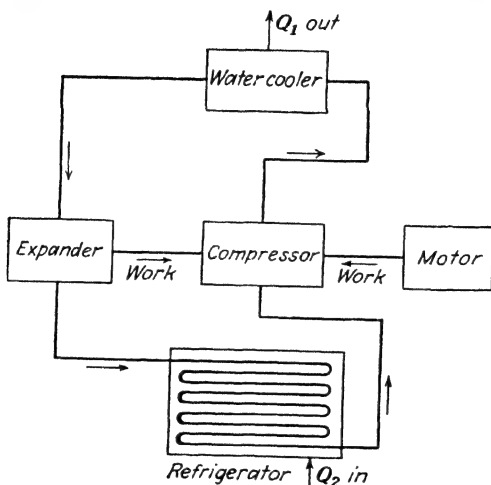
FIG. X.3.—Gas-expansion process of refrigeration.

it absorbs heat at constant pressure, and the warmer gas returns to the compressor intake to complete the cycle.   In certain adaptations of this process, the gas leaving the refrigerator may not be recycled, but the principle is the same.

It is important to note that the compressed gas must be caused to do external work by expansion in an engine.   From the discussion in Chap. VII it should be evident that a throttle or Joule-Thomson expansion would produce a much smaller refrigerating effect and would result in a very inefficient cycle as compared with the one with engine expansion. It is true that the Joule-Thomson effect may be used as the sole source of refrigeration in processes operating at very low temperatures, but this requires much higher pressures.

FIG.   X.4.—Gas-expansion refrigeration cycle on a temperature-entropy diagram.

The idealized cycle is represented on a TS diagram in Fig. X.4. T_0 represents the temperature of the cooling water and T_2 the temperature

to be maintained in the refrigerator (both assumed constant to simplify the analysis); AB represents the adiabatic (and isentropic in the ideal case) compression of the gas; BC represents the constant-pressure change in the water cooler, CD the adiabatic expansion, and DA the constant-pressure absorption of heat in the refrigerator. The cycle as drawn is clearly less efficient than the Carnot cycle between the given temperature limits T_0 and T_2. To remove the heat corresponding to the area under DA down to the $T = 0$ axis, the work required is given by area $ABCD$. The Carnot cycle removes a greater amount of heat (area under EA) with less work (area $AECF$). To operate on the Carnot cycle it would be necessary to accomplish a part of the compression and of the expansion isothermally. This is very difficult to achieve in any practical device.

Assuming constant specific heats, the heats absorbed and rejected are given, respectively, by the two equations

$$Q_2 = wC_p(T_A - T_D) \tag{X.13}$$
$$Q_1 = wC_p(T_B - T_C) \tag{X.14}$$

where $w =$ pounds of gas circulated per unit of time. The theoretical work required per unit of time (power) for adiabatic compression is given by Eq. (VII.31), which for this case may be written

$$W \text{ (compression)} = \frac{k}{k-1}\left(\frac{w}{M}\right)RT_A\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right] \tag{X.15}$$

Since, by Eq. (III.59), $\qquad R = \dfrac{k-1}{k}MC_p$

Eq. (X.15) can also be written

$$W = wC_pT_A\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right] \tag{X.16}$$

Similarly, the theoretical work obtained from the expansion is

$$W = -wC_pT_D\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right] \tag{X.17}$$

p_1 is the lower pressure in all cases. The net work for the cycle is the algebraic sum of Eqs. (X.16) and (X.17), or

$$W \text{ (net)} = wC_p(T_A - T_D)\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right] \tag{X.18}$$

The net work must also be given by

$$W = Q_1 - Q_2 \tag{X.3}$$
$$W = wC_p[(T_B - T_C) - (T_A - T_D)] \tag{X.19}$$

From Eqs. (X.13), (X.18), and (X.19) the following two expressions for coefficient of performance are obtained:

$$\beta = -\frac{T_A - T_D}{(T_A - T_D) - (T_B - T_C)} \qquad (X.20)$$

$$\beta = \frac{1}{(p_2/p_1)^{\frac{k-1}{k}} - 1} \qquad (X.21)$$

The gas-expansion cycle is no longer of much practical importance, but it is worth this brief discussion because it illustrates some important principles and because it is important to show why it has been so largely superseded by the vapor-compression process in spite of the great advantage that the working fluid can be air, which is available without cost and does not possess the other objectionable properties of many refrigerating fluids such as corrosiveness, inflammability, and irritating or toxic effect. Furthermore, the same general principle does find application in low-temperature gas-separation processes and in some solvent-recovery processes. The following concrete illustration will serve to bring out some of the fundamental difficulties with this cycle.

Illustration 3.—An air refrigerating machine is to be used to maintain a space at 10°F. and must absorb heat at the rate of 1,000 B.t.u. per min. Cooling water is available at 70°F. What are the power required, the coefficient of performance, and the compressor displacement if the compressor takes in air at normal barometer and compresses it to 75 lb. per sq. in. abs.?

Under ideal conditions there would be no difference in temperature between the air and the space being refrigerated at the point where the air leaves the refrigerator and between the air and the cooling water at the point where the air leaves the cooler, and this fixes T_A and T_C. Thus,

$$T_A = 459.7 + 10 = 469.7°R.$$

and

$$T_C = 459.7 + 70 = 529.7°R.$$

From Eq. (VII.23),

$$T_B = 469.7\left(\frac{75}{14.7}\right)^{\frac{1.40-1}{1.40}} = 748°R.$$

and

$$T_D = 529.7\left(\frac{14.7}{75}\right)^{\frac{1.40-1}{1.40}} = 332°R.$$

$$= -127.7°F.$$

Assuming C_p for air is constant at 0.24, the weight of air to be circulated per minute is, from Eq. (X.13),

$$w = \frac{1,000}{0.24(469.7 - 332.0)} = 30.3 \text{ lb./min.}$$

The net theoretical work, by Eq. (X.19), is

$$W = 30.3 \times 0.24[(748 - 529.7) - (469.7 - 332)] = 590 \text{ B.t.u./min.} = 13.9 \text{ hp.}$$

Horsepower per ton $= 13.9/5 = 2.78$. The coefficient of performance $= 1,000/590 =$

1.69. The coefficient of performance for a Carnot cycle between the same limits is

$$\frac{T_A}{T_A - T_C} = 7.82$$

and so we see that this cycle, even when ideally operated, departs very considerably from the Carnot cycle.

The volume of air entering the compressor is

$$\frac{30.3}{29} \times 359 \times \frac{469.7}{491.7} \text{ cu. ft./min.} = 358$$

Neglecting the effect of clearance, the displacement per ton of refrigeration is

$$\frac{358}{5} = 71.5 \text{ cu. ft./min.}$$

To obtain a figure more representative of practice conditions, let us assume a minimum of 10°F. temperature difference at the water cooler and at the refrigerator and over-all power efficiencies of 80 per cent and 70 per cent for the compressor and expander, respectively (the expander is less efficient because of the low temperature at which it operates). Then,

$$T_A = 459.7, \qquad T_C = 539.7$$
$$= 460 \qquad = 540$$

Assume that 85 per cent of the theoretical temperature drop is obtained in the expander. Calculating the theoretical drop by Eq. (VII.23) and taking 85 per cent of it,

$$T_D = 369°R.$$

By Eq. (X.13), $\qquad w = 46.0 \text{ lb./min.}$

The work of compression calculated by Eq. (X.16) and multiplied by $1/0.80$ is

$$W = 3,760 \text{ B.t.u./min.}$$

The work of expansion calculated by Eq. (X.17) and multiplied by 0.70 is

$$W = 1,690 \text{ B.t.u./min.}$$
$$\text{Net work} = 2,070 \text{ B.t.u./min.}$$
$$= 48.7 \text{ hp.}$$
$$= 9.73 \text{ hp./ton}$$
$$\beta = \frac{1,000}{2,070} = 0.48$$

This is believed to be the order of the figures obtained in actual practice though actual data on air systems are very meager. It is of interest to note the very great effect on the coefficient of performance of the few irreversible effects that were assumed. An ammonia refrigerating machine performing the same service will give a much higher coefficient, as will be shown later.

From Eq. (X.21) it is evident that the coefficient of performance is increased by decreasing the pressure ratio. The limit would be reached when

$$\frac{p_2}{p_1} = \left(\frac{T_C}{T_A}\right)^{\frac{k}{k-1}} = \left(\frac{T_0}{T_2}\right)^{\frac{k}{k-1}} \qquad (X.22)$$

which corresponds to a coefficient equal to that of the Carnot cycle.   At
this limit, $T_B = T_C$ and $T_D = T_A$, and we see from Eqs. (X.13) and
(X.14) that a very large amount (infinite at the limit) of gas would have
to be circulated.   In other words, any increase in the coefficient of
performance of this cycle must be made at the expense of an increase
in the displacement of the compressor and expander.   As will be shown
later (page 432), the displacement per ton in Illustration 3 is already very
high in comparison with that for a vapor-compression cycle.   This diffi-
culty can be partly overcome by operating the cycle at a higher pressure
level.   Thus, by choosing a compressor suction pressure of 75 lb. per sq.
in. abs. and a discharge pressure of 382 lb. per sq. in. abs., the coefficient
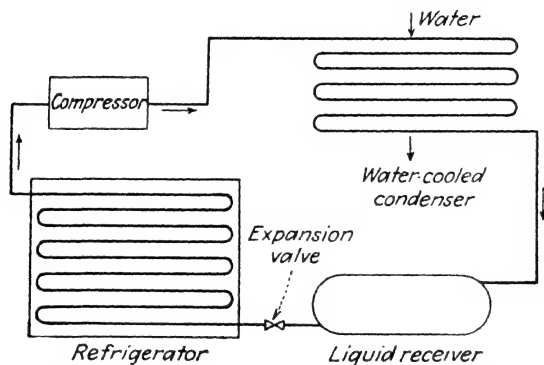
Fig. X.5.—Diagram showing elements of a simple vapor-compression refrigeration cycle.

of performance would be the same as that for the cycle of Illustration 3,
but the compressor displacement would have to be only one-fifth as
great.   A refrigeration system using air with low and high pressures
of about 65 and 240 lb. per sq. in. abs., respectively, known as the
"Allen dense-air system," was at one time used extensively for marine
refrigeration, but it has now been almost entirely supplanted by the
vapor-compression systems.

Vapor-compression, or Two-phase, Process.—In Fig. X.5 the refrig-
erating fluid is compressed to such a pressure that it will condense to a
liquid when cooled by water at constant pressure.   The liquid leaving
the condenser is temporarily stored in a receiver, from which it flows to an
expansion valve, where it is throttled to the lower pressure existing in
the coils of the refrigerator.   The liquid evaporates at this lower pres-
sure, absorbing heat, and the vapor returns to the suction side of the
compressor and is then recycled.   The heat to be removed in the refrig-
erator may be absorbed directly by the evaporating fluid or indirectly
by an intermediate fluid such as a brine that is continuously circulated
between the space to be refrigerated and an evaporator or brine cooler.

The direct system is always preferable if it can be used, but in those cases where all possibility of a leak of refrigerant into the space being cooled must be avoided or where one refrigerating machine is to serve for cooling at several widely separated points the indirect system must be used.

With the aid of Fig. X.6 the ideal cycle of changes may be followed on a TS diagram. Point A represents saturated liquid at temperature T_0, the temperature of the cooling water, and at pressure p_2, the condition at which the liquid comes to the expansion valve. The throttling expansion to the lower pressure p_1 existing in the refrigerator is shown by the constant H line AB.* It is at once evident from the diagram that the expansion results in a partial vaporization of the liquid, the fraction of vapor (quality) being given by the ratio of FB to FC. The remainder of the liquid then vaporizes in the refrigerator at the constant suction pressure of the compressor and hence at constant temperature, as indicated by the line BC. In this case, the vapor leaving the refrigerator is assumed to be saturated, but it could just as well have been assumed to be slightly wet or even superheated without changing the general picture. CD represents adiabatic compression of the vapor back to the pressure

Fig. X.6.—Vapor-compression cycle on a temperature-entropy diagram.

p_2. The superheated vapor is then cooled at constant pressure along DE and condensed to a liquid along EA, completing the cycle. The two pressures in the cycle are fixed by the respective temperatures, which, in turn, are fixed by the cooling-water temperature and the temperature that one desires to maintain in the refrigerator.

Comparison of this cycle with the Carnot cycle shows two reasons why it is less efficient, *viz.*, (1) the irreversible expansion AB and (2) the superheating to a temperature higher than T_0. The first source of inefficiency could be removed, in principle at least, by expanding in an engine (line AG) instead of a valve. The second source of cycle inefficiency could be eliminated by allowing the evaporation in the refrigerator to proceed only to C' and thus admit wet vapor to the compressor, the resultant change of state in adiabatic compression being indicated by $C'E$. Such "wet compression" has been practiced, but the practical gain is too small to outweigh the operating difficulties.

The loss in efficiency due to the expansion along AB can be partly overcome by expanding in more than one stage, separating the vapor from

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* This is shown as a dashed line because, being an irreversible process, the actual path is not definitely fixed. One knows only the terminal states.

the liquid, and recompressing each vapor separately. Actually, the irreversible effects in the ideal ammonia-compression cycle operating under average conditions cause an increase in power over that of the Carnot cycle of only 15 to 20 per cent. Thus, the opportunities for power reduction are not great, and the savings would generally be more than offset by the complication of the apparatus.

Analysis of Vapor-compression Cycle.—It will be interesting to analyze this cycle quantitatively and to compare it both ideally and practically with the gas-compression cycle.

For this purpose a Mollier chart is somewhat more convenient than a TS diagram; that with coordinates of log p and H is commonly used. In Fig. X.7, the vapor-compression cycle is shown on an outline of such
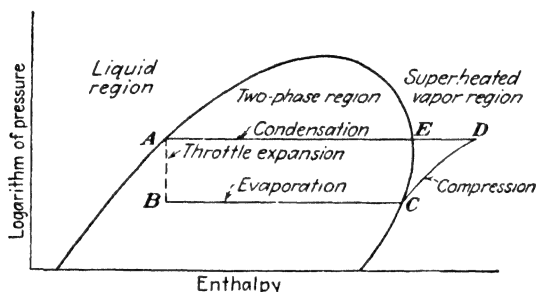
Fig. X.7.—Vapor-compression process on a Mollier diagram.

a chart, the various points being lettered to correspond with the analogous points on the TS diagram of Fig. X.6.

Using subscripts to correspond to the respective points in Figs. X.6 and X.7 we shall deal with the following quantities:

Basis: 1 lb. of fluid.

$$\text{Heat absorbed in refrigerator} = Q_2 = H_C - H_B \qquad \text{(X.23)}$$
$$\text{Heat given up in condenser} = Q_1 = H_D - H_A \qquad \text{(X.24)}$$

(Note that D and E may coincide if wet vapor is compressed.)

$$\text{Work required} = Q_1 - Q_2 = H_C - H_B - H_D + H_A = H_C - H_D \qquad \text{(X.25)}$$

(since $H_A = H_B$).

$$\text{Coefficient of performance} = \frac{H_C - H_B}{H_D - H_C} \qquad \text{(X.26)}$$

The various enthalpies can be readily obtained from thermodynamic tables or diagrams. If the usual tabulation or graph of thermodynamic properties is not available, the heat quantities can be calculated from data on specific heat and latent heat and the work from the equations developed in Chap. VII. The amount of refrigerant (working fluid) needed

to be circulated per minute per ton of refrigeration is given by

$$w \text{ (lb./min.)} = \frac{200}{H_C - H_B} \qquad \text{(X.27)}$$

when enthalpy is expressed in B.t.u. per pound. The compressor displacement (neglecting clearance) per ton is given by,

$$V \text{ (cu. ft./min.)} = wv_c$$

where v_c is the specific volume of the refrigerant at the state in which it enters the compressor.

$$\text{Hp./ton} = \frac{12,000}{2,545\beta} = \frac{4.713}{\beta} \qquad \text{(X.28)}$$

With the aid of Eqs. (X.23) to (X.28) and tables of thermodynamic properties we are in a position to compare quantitatively various refrigerating cycles operating on the vapor-compression process, among themselves, and also with the gas-expansion process. We may study the effect of such variables as (1) nature of working fluid, (2) temperature of cooling water, (3) temperature desired in the refrigerator, and (4) wet vs. dry compression. Although the calculations are made for ideally operated cycles, nevertheless the general conclusions will also be valid for practical cycles. Departures from ideal operation will be briefly treated later (page 435).

Illustration 4.—Compare the vapor-compression process using ammonia as refrigerant with the gas-expansion process, taking the same conditions as in Illustration 3.

At 10°F. the vapor pressure of NH_3 = 38.5 lb. per sq. in. abs., and this will be the pressure on the low-pressure side of the expansion valve. The high pressure will be the vapor pressure at 70°F., or 128.8 lb. per sq. in.

From ammonia tables,[1] $H_A = 120.5 = H_B$
  H_C (assuming dry saturated vapor from the refrigerator) = 614.9
  $S_C = 1.3157$
H_D = heat content of superheated vapor at 128.8 lb./sq. in. pressure and with an entropy of 1.3157 = 687.2

$$\beta = \frac{614.9 - 120.5}{687.2 - 614.9} = 6.93$$

$$\text{Hp./ton} = \frac{4.713}{6.93} = 0.681$$

$$\text{Lb. } NH_3 \text{ circulated per min.} = \frac{1,000}{614.9 - 120.5} = 2.03$$

$$\text{Hp. required} = \frac{2.03(614.9 - 687.2)60}{2,545} = 3.45$$

$$v_c = 7.304$$

Compressor displacement = 2.03 × 7.304 = 14.80 cu. ft./min. or 2.96 cu. ft./min./ton

[1] PERRY, J. H., editor, "Chemical Engineers' Handbook," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941. Units are B.t.u., pounds, cubic feet, and degrees Fahrenheit.

The great superiority of the vapor-compression process over the gas-expansion process is at once evident from inspection of the following tabulation, summarizing some of the results calculated in Illustrations 3 and 4:

Item	Vapor compression using NH₃	Air expansion with intake at atmospheric pressure
Coefficient of performance..............	6.93	1.69
Hp. per ton of refrigeration.......	0 681	2.78
Compressor displacement, cu. ft./min./ton	2.96	71.5

These figures are for the ideal operation of the processes, but the comparison would not be appreciably changed under actual operating conditions.

With the usual dense-air system the air-compressor displacement would, of course, be much less, but even so it would have to be much larger than that of the ammonia compressor.

Comparison of Refrigerants.—Following the methods just illustrated, a comparison can be made between different refrigerating mediums that reveals some interesting facts.   In Table X.1, there is given a comparison made in this way for the following specific case:[1]

1. Evaporation temperature of 5°F.
2. Condensing temperature of 86°F.
3. Liquid comes to expansion valve without subcooling.
4. Vapor entering compressor is saturated.

Isentropic compression was assumed, and most of the thermodynamic pioperties were taken from the tables in the "Chemical Engineers' Handbook."   The data on methylene chloride in Table X.1 were taken from an article by R. W. Waterfill.[2]   Some of the properties were taken from the "Refrigerating Data Book."[3]   For a similar tabulation the reader is referred to a paper by Macintire.[4]

If operated on the Carnot cycle there would, of course, be no difference in the coefficients of performance of the various fluids.   Since

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[1] These conditions differ slightly from the standard ones chosen by the American Society of Refrigerating Engineers (A.S.R.E.) for rating refrigerating machines.   Its standard has the same evaporation and condensing temperature as given above; but the liquid to the expansion valve is subcooled 9°F., and the vapor entering the compressor is superheated 9°F.

[2] WATERFILL, R. W., *Ind. Eng. Chem.*, **24**, 616 (1932).

[3] Third edition, American Society of Refrigerating Engineers, New York, 1936. fifth edition (1943–1944) is now available.

[4] MACINTIRE, H. J., *Chem. Met. Eng.*, **45**, 682 (1938).

TABLE X.1.—COMPARISON OF REFRIGERANTS

Based on 1 ton of refrigeration in ideally operated cycle with 5°F. evaporation temperature and 86°F. condensing temperature

Refrigerant	Evaporation pressure, lb./sq. in. abs.	Condensing pressure, lb./sq. in. abs.	Sp. vol. at compressor intake, cu. ft./lb.	Lb. circulated per min.	Vol. to compressor, cu. ft./min.	Coefficient of performance	Horse-power	Per cent of Carnot efficiency	Remarks
Any fluid in Carnot cycle	......	......	......	......	......	5.74	0.821	100	
Carbon dioxide	334.4	1,039	0.267	3.53	0.94	2.56	1.84	44.7	
Ammonia	34.3	169.2	8.151	0.413	3.36	4.85	0.973	84.5	
Propane	41.9	155.3	2.48	1.65	4.10	4.88	0.967	85.0	
Dichlorodifluoromethane	26.5	107.9	1.485	3.92	5.83	4.72	0.997	82.3	Also known as F-12 or Freon-12
Methyl chloride	20.9	95.5	4.53	1.42	6.45	4.67	1.007	81.7	
Sulphur dioxide	11.8	66.5	6.42	1.41	9.06	4.74	0.995	82.5	
Ethyl chloride	4.65	27.1	17.1	1.40	24.0	5.32	0.888	92.7	
Diethyl ether	1.5	12.3	35.0	1.58	55.5	4.86	0.971	84.6	
Methylene chloride	1.17	10.1	50.6	1.48	74	4.90	0.965	85.0	Also known as Carrene
Dichloroethylene	0.82	7.0	63.7	1.75	111	5.14	0.918	89.4	Also known as Dieline
Trichloroethylene	0.156	1.82	231	2.18	505	5.09	0.928	88.5	Also known as Trieline

the vapor-compression cycle does not depart greatly from the Carnot cycle, we should not expect to find great differences between the power requirements to produce a ton of refrigeration with different fluids. Reference to Table X.1 shows this to be the case with the exception of carbon dioxide, where the departure from the Carnot cycle is greater because the condensing temperature is so close to the critical temperature of CO_2. There are various ways in which the efficiency of the CO_2 cycle can be increased, but all at the expense of complication of the process. This point will receive further elaboration later in this chapter.

Study of the table also reveals the reason why ammonia has been used almost exclusively for commercial refrigeration. Its performance coefficient is good, and it requires the smallest compressor displacement with the single exception of CO_2, which is generally ruled out for commercial use because of the high pressures and the low efficiency. It will be noticed that Freon-12 (dichlorodifluoromethane), which is increasing in popularity, is quite similar to ammonia in its thermodynamic properties and has the advantage of being safer to use since it is nonirritant, nontoxic, and nonexplosive. Propane is also very similar to ammonia but has the disadvantage of forming explosive mixtures with air.

Water vapor is the ideal refrigerant from the standpoint of safety and cheapness, but it cannot be used for temperatures below 40°F. and hence was not included in the table. When used for refrigeration in the range from room temperature to 40°F., it compares favorably with other fluids in coefficient of performance, but the very large volumes to be handled—476 cu. ft. per min. per ton for 40°F. evaporation temperature and 86°F. condensing temperature—require the use of centrifugal or steam-jet compressors.

For small units such as those used in households, SO_2, ethyl chloride, and methyl chloride have been preferred to ammonia because of the lower pressures and lesser irritating effect and the fact that copper-containing metals can be used in the construction of the machines.

It may be noted that it is desirable to have the low-pressure side of the system at a pressure somewhat greater than atmospheric in order to prevent the infiltration of air, which will cause trouble as a result of both its own presence and that of accompanying water vapor. This is one disadvantage of SO_2 and other low-vapor-pressure refrigerants. This requirement also makes it disadvantageous to use ammonia refrigeration below −25°F. To evaporate ammonia much below this temperature would necessitate a suction pressure below atmospheric, and this has generally been considered in the past to be bad practice.[1]

[1] In recent years, however, efficient leakproof seals for shafts have been developed, and it is now fairly common to operate small units at suction pressures well below atmospheric. Freon refrigerating machines are operating at pressures as low as

In some applications, such as air conditioning of theaters, public buildings, etc., or marine refrigeration, refrigerants such as NH_3 and SO_2 with toxic, explosive, irritating, or other properties constituting a serious hazard cannot be used. For such cases, carbon dioxide, methylene chloride, and ethyl chloride have been extensively used in the past but will probably be largely supplanted by the chlorofluoromethanes (dichlorodifluoromethane is only one of several of these halogen-substituted methanes that are available as refrigerants).

Actual vs. Theoretical Power Requirement.—In the actual refrigerating process, allowance must be made for the necessary temperature differences to cause economical heat transfer, for heat leakage from the surroundings, friction and other losses in the compressor, and for other minor irreversible effects. For most cases one can make a reasonable assumption about the temperature differences and estimate the temperatures at which the fluid is to be evaporated and condensed. If the heat is absorbed, not directly by the evaporating refrigerant, but indirectly through the use of a circulating brine as is sometimes necessary, the overall temperature difference, and hence the power, will be increased.

The power for compression, as calculated from the usual formula or obtained from thermodynamic properties on the assumption of isentropic compression, approximates the actual indicated power of the compressor. Allowing 80 per cent efficiency from brake horsepower to indicated horsepower and about 93 per cent efficiency for the motor and drive, we arrive at an over-all efficiency of 75 per cent for the compressor, which is suggested for use in approximate estimation of the power requirement.

Illustration 5.—Fifteen hundred gallons of a solution of specific gravity = 1.15 and specific heat = 1.05 B.t.u. per lb. per °F. is to be cooled per hour from 7 to 0°F., using direct ammonia expansion. Cooling water is available at 65°F. under the worst conditions and is to rise 15°F. in the condenser. Estimate the size of refrigerating unit required and the amount of power expressed in kilowatts.

Heat to be absorbed = $1,500 \times 8.33 \times 1.15 \times 1.05 \times 7 = 105,800$ B.t.u./hr.

In addition to this heat there will be a certain amount of heat that leaks in from the surroundings. This might be estimated if the details of a specific installation were known, but if the system is well insulated this leakage will be small and can usually be neglected. To make some allowance for it, we shall round off the above figure to 110,000 B.t.u. per hr.

$$\text{Tons of refrigeration} = \frac{110,000}{12,000} = 9.2$$

A minimum temperature difference of 10°F. in the ammonia condenser and 10°F. in the refrigerator will be assumed. This is a purely arbitrary assumption but is probably sufficiently close to practical conditions for our present purpose. This

1 lb. per sq. in. abs. and producing temperatures as low as −100°F., and even lower in some cases.

assumption fixes the ammonia condensing temperature at 90°F. and the evaporation temperature at −10°F. The corresponding pressures are 180.6 and 23.7 lb. per sq. in. abs., respectively

Taking all properties from the "Chemical Engineers' Handbook,"

$$\text{Enthalpy of liquid NH}_3 \text{ at } 90°F. = 143.5 \text{ B.t.u./lb.}$$
$$\text{Enthalpy of NH}_3 \text{ vapor at } -10°F. = 608.5$$
$$\text{Lb. NH}_3 \text{ to be circulated per hr.} = \frac{110,000}{608.5 - 143.5} = 237$$

Enthalpy of superheated NH_3 vapor at 180.6 lb. per sq. in. abs. having the same entropy as saturated vapor at −10°F. = 738.7

$$\text{Theoretical power for compression} = (608.5 - 738.7)237 = 30,800 \text{ B.t.u./hr.}$$
$$= \frac{30,800}{3,415} \text{ or } 9.03 \text{ kw.}$$
$$\text{Estimated actual power} = \frac{9.03}{0.75} = 12.03 \text{ kw.}$$

The theoretical power for the Carnot cycle operating between the given temperature limits of 0 and 65°F. would be

$$\frac{110,000 \times 65}{3,415 \times 460} = 4.56 \text{ kw.}$$

Thus, for a quick, rough estimate of the power requirement for a given cooling process, it is recommended that the Carnot cycle power be calculated; the lowest temperature desired in the refrigerator and the cooling-water temperature should be taken as temperature limits. Then a 40 per cent over-all efficiency for the actual cycle, based on the Carnot as the standard, should be assumed.

Rating of Refrigerating Equipment.—The rated capacity of any refrigerating unit is commonly expressed in terms of tons of refrigeration per 24 hr. Since this will depend on the conditions of operation, it is necessary to take certain arbitrary conditions as the standard ones on which to base the rating. The standard conditions adopted by the A.S.R.E. were given on page 432. It is important for the user of such equipment to realize how markedly the capacity can change with operating conditions and that he will not get the rated capacity if the conditions are materially different from the standard ones. This can best be shown by a numerical example.

Illustration 6.—An ammonia refrigerating unit is rated at 50 standard tons. The compressor has a double-acting cylinder, 10 × 12 in., and runs at 180 r.p.m., and the clearance is taken to be 5 per cent. What would be the capacity of the unit in tons of refrigeration if the evaporation temperature of the ammonia were −10°F. and the condensing temperature 100°F.? Assume that liquid at the expansion valve is not subcooled and saturated vapor enters the compressor.

At −10°F.:

$$\text{Pressure} = 23.7 \text{ lb./sq. in.}$$
$$v \text{ of saturated vapor} = 11.50 \text{ cu. ft.}$$
$$H \text{ of saturated vapor} = 608.5 \text{ B.t.u./lb.}$$

At 100°F.:
$$\text{Pressure} = 211.9 \text{ lb./sq. in.}$$
$$H \text{ of liquid} = 155.2$$
$$\text{Refrigerating effect per lb.} = 608.5 - 155.2 = 453.3 \text{ B.t.u.}$$
$$\text{Cylinder displacement} = \frac{0.785 \times 100 \times 2 \times 12 \times 180}{1,728} = 196 \text{ cu. ft./min.}$$

By Eq. VII.39,

$$\text{Volumetric efficiency} = 1 + c - c \left(\frac{p_2}{p_1}\right)^{\frac{1}{k}} = 1 + 0.05 - 0.05 \left(\frac{211.9}{23.7}\right)^{\frac{1}{1.30}} = 0.78$$
$$\text{Intake volume} = 0.78 \times 196 = 153 \text{ cu. ft./min.}$$
$$\text{Lb. NH}_3 \text{ per min.} = \frac{153}{11.50} = 13.3$$
$$\text{Tons of refrigeration} = \frac{13.3 \times 453.3}{200} = 30.2$$

The assumed change in operating conditions from those of the standard rating caused the rated capacity to drop from 50 to 30 tons.

VARIANTS OF THE SIMPLE VAPOR-COMPRESSION PROCESS

Stage Compression and Expansion.—The chemical industry is more and more finding need for temperatures as low as −50°F. and even lower. When evaporation temperatures below about −15°F. are to be used with an ammonia system, the pressure ratio for compression is great enough so that compression in more than one stage becomes desirable. Thus, with an evaporation temperature of −15°F. and condensing temperature of 85°F., the pressure ratio in the compressor must be 8, which is about the limit for single-stage compression. The reasons for the use of stage compression are essentially the same as for gas compression, discussed in Chap. VII. An additional advantage lies in the fact that refrigeration can be obtained at more than one temperature level. The system differs from that used in gas compression in that it is not feasible to cool the compressed vapor in an intercooler back to the initial temperature and that more than two stages are seldom used. Two-stage systems can be used to about −70°F., and three-stage systems are being used to obtain refrigeration at temperatures as low as −120°F.

As in gas compression the two-stage compression-refrigeration system may consist merely of two compression cylinders with intermediate water cooling. The amount of intercooling obtained with water is, of course, limited by the water temperature, but further cooling is sometimes obtained by injecting liquid ammonia into the compressed vapor. A further gain is possible by expanding the liquid ammonia in two stages instead of one, thus reducing the amount of vapor that must be compressed in the low-pressure stage. A diagram of a two-stage system utilizing all these various possibilities is shown in Fig. X.8. Vapor from the refrigerator *J* enters the low-pressure stage *A* of the compressor;

the compressed vapor is water-cooled in *B* and further cooled in *C* by evaporation of liquid ammonia injected into it. Vapor from *C* is compressed in the high-pressure stage *D*, cooled and condensed to a liquid by water cooling in *E*, and expanded in valve *F* into the accumulator *G* maintained at the interstage pressure. The vapor formed by the Joule-Thomson expansion is returned to cylinder *D*, and the liquid divides, one part expanding through *H* into the refrigerator *J* to produce the desired refrigeration and another portion being diverted to act as a cooling
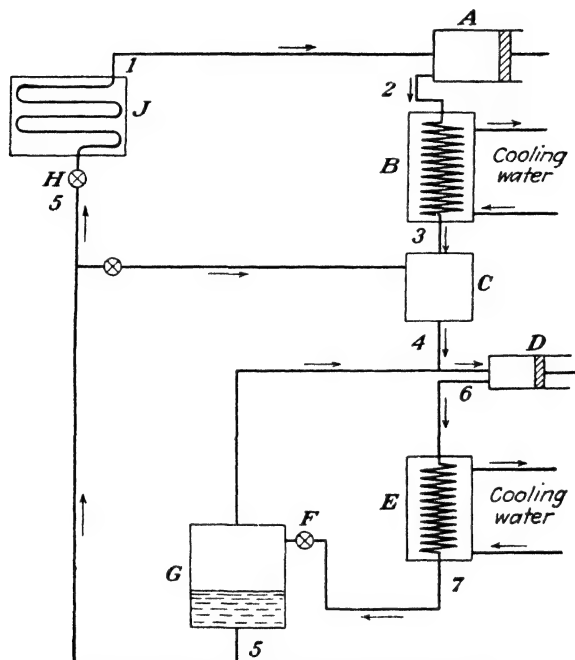
Fig. X.8.—Two-stage compression and expansion.

medium in *C*. The first stage of compression is often accomplished in a separate machine known as a "booster compressor" because this permits greater flexibility in choice of conditions.

The analysis of the ideal cycle of Fig. X.8 to determine the possible performance with various refrigerants and with various operating conditions is an interesting problem that can readily be solved with the aid of a table or diagram of the thermodynamic properties of the refrigerant in question. A paper by Macintire[1] analyzes such a process quantitatively for a specific case using ammonia as the refrigerant.

[1] MACINTIRE, *op. cit.*

Binary Fluid Cycle.—When temperatures below about $-15°F$. are to be produced, the stage compression system previously described may be used. Theoretically, the lower limit of temperature is fixed only by the triple point of the refrigerant (at this temperature, solid will be formed), which for ammonia is about $-108°F$. Practically, however, difficulties may be encountered if the pressure on the suction side of the compressor is less than atmospheric, and this sets a limit of $-28°F$. to the evaporation temperature of ammonia. This limit may be lowered by using a refrigerant such as CO_2 (triple point about $-70°F$.), but then the pressure in the condenser is very high if water cooling is used. This may be avoided by the use of a cycle using two refrigerants, sometimes referred to as "split-stage compression."[1] This consists merely in two simple compression cycles operating together so that the refrigerant of higher vapor pressure is condensed by transferring its heat to evaporating liquid of the other refrigerant, which in turn is condensed by water cooling. Thus, if refrigeration were to be performed at $-60°F$. and the cooling-water temperature was such that condensation at $85°$ were feasible, a combination of CO_2 and NH_3 cycles might be used. Assuming evaporation of CO_2 at $-60°F$. and of ammonia at $0°F$. and allowing $10°F$. temperature difference between condensing CO_2 and evaporating ammonia, the pressure conditions of the binary fluid cycle compared with cycles using each fluid alone are as follows:

	Suction pressure lb./sq. in. abs.	Condenser pressure lb./sq. in. abs.
Binary cycle:		
CO_2 pressures............	94.7	360
NH_3 pressures...........	30.4	166
CO_2 cycle....	94.7	1,027
NH_3 cycle................	5.55	166

Illustration 7.—Compare by means of a thermodynamic analysis the two-stage system shown in Fig. X.8 using ammonia as refrigerant with the binary fluid cycle using ammonia and carbon dioxide. The conditions and assumptions to be used for a specific case are as follows:

Refrigerant to be evaporated at $-60°F$.

Fluids leave water-cooled condensers or coolers at $85°F$.

Compression is isentropic.

Vapors entering compressors are saturated at the given suction conditions.

$10°F$. temperature difference between condensing CO_2 and evaporating NH_3 in the binary cycle.

Interstage pressure in the two-stage process to be such that approximately equal work is done in the stages.

[1] When used to produce very low temperatures, generally with three or more refrigerating mediums, this kind of a cycle is commonly called a "cascade."

Neglect all heat leakage and neglect pressure drop due to friction except at the throttle expansions.

In the binary cycle, the ammonia is to be evaporated at 0°F.

Ammonia proper'ies from "Chemical Engineers' Handbook."

Carbon dioxide properties from *TS* chart of Liquid Carbonic Corporation based on data of Planck and Kuprianoff. (See Appendix.)

All enthalpies in B.t.u. per pound.

All entropies in B.t.u. per pound per degree Rankine.

1. *Two-stage Compression.*

Quantity basis: 1 lb. NH_3 passing through refrigerator coils.

$$\text{Suction pressure} = 5.55 \text{ lb./sq. in. abs.}$$
$$\text{Discharge pressure} = 166.4 \text{ lb./sq. in. abs.}$$

The interstage pressure for equal work can be calculated by trial. A few trials indicate that 40 lb. per sq. in. abs. is approximately correct, and this figure will be assumed.

Ammonia properties to be used are as follows:

State	p, lb./sq. in. abs.	t, °F.	S	H	Notes
1. Saturated vapor	5.55	−60	1.4769	589.6	
2. Superheated vapor .	40	174	1.4769	705.2	Isentropic compression from state 1
3. Superheated vapor	40	85	. . . .	657.1	
4. Saturated vapor	40	11.7	1.3125	615 4	
5. Saturated liquid	40	11.7	. . . . .	55.6	
6. Superheated vapor	166.4	193	1.3125	703.0	Isentropic compression from state 4
7. Saturated liquid	166.4	. . .	. .	137.4	
8. Saturated vapor	30 4	0	1.3352	611.8	
9. Superheated vapor . .	166 4	. .	1 3352	718.4	Isentropic compression from state 8

NOTE: State numbers 1 to 7 correspond to those in Fig. X.8. States 8 and 9 are states in the binary cycle.

Refrigeration per lb. NH_3 in refrigerator $= H_1 - H_5 = 589.6 - 55.6 = 534$ B.t.u.

Heat removed in exchanger C, Fig. X.8 $= H_3 - H_4 = 657.1 - 615.4 = 41.7$ B.t.u.

$$\text{Lb. } NH_3 \text{ required for this cooling} = \frac{H_3 - H_4}{H_4 - H_5} = \frac{41.7}{615.4 - 55.6} = 0.0745$$

Let x = quality of NH_3 after expansion at F.

$$\text{Heat balance around } F: H_7 = xH_4 + (1 - x)H_5$$
$$137.8 = 615.4x + 55.6(1 - x)$$
$$x = 0.147$$

Let m — lb. NH_3 entering second stage.

$$m = 1.00 + 0.0745 + 0.147m$$
$$m = 1.260$$

Work of first stage $= H_2 - H_1 = 705.2 - 589.6 = 115.6$ B.t.u.
Work of second stage $= m(H_6 - H_4) = 1.260(703 - 615.4) = 110$ B.t.u.
Total work $= 225.6$ B.t.u./lb. NH_3
Power per ton of refrigeration $= 225.6 \times \frac{200}{534} = 84.6$ B.t.u./min. $= 2.00$ hp.

$$\text{Coefficient of performance} = \frac{534}{225.6} = 2.37$$

Displacement of first stage of compressor (100 per cent volumetric efficiency) per ton
$$= 44.73 \times \frac{200}{534} \text{ cu. ft./min.} = 16.8$$

2. *Binary Fluid Cycle.*
Basis: 1 lb. CO_2.
Carbon dioxide properties are as follows:

State	p	t	S	H	Notes
10. Saturated vapor.........	95	−60	1.265	278	
11. Superheated vapor... ...	360	10	1.265	304	Isentropic compression from state 10
12. Saturated liquid.........	360	10	.....	167	

State 10 is that of CO_2 leaving the refrigerator and entering the compressor.
State 11 is that of CO_2 leaving the compressor.
State 12 is that of liquid CO_2 leaving the ammonia-cooled condenser and entering the expansion valve.

Refrigerating effect $= H_{10} - H_{12} = 278 - 167 = 111$ B.t.u.
Work of CO_2 compressor $= H_{11} - H_{10} = 304 - 278 = 26$ B.t.u.
Heat removed in ammonia-cooled condenser $= H_{11} - H_{12} = 304 - 167 = 137$
Heat absorbed by 1 lb. ammonia $= H_8 - H_7 = 611.8 - 137.4 = 474.4$

$$m = \text{lb. } NH_3 \text{ per lb. } CO_2 = \frac{137}{474.4} = 0.289$$

Work of NH_3 compressor $= m(H_9 - H_8) = (718.4 - 611.8)0.289 = 30.8$ B.t.u.
Total work $= 56.8$ B.t.u.
Power per ton refrigeration $= 56.8 \times \frac{200}{111} = 102.2$ B.t.u./min. $= 2.42$ hp.

$$\text{Coefficient of performance} = \frac{111}{56.8} = 1.96$$

Theoretical displacement of the CO_2 compressor $= \frac{200}{111} \times 0.927 = 1.67$ cu. ft./min.

From these calculations it is concluded that the two-stage cycle using ammonia has a definite thermodynamic advantage over the binary fluid cycle using ammonia and carbon dioxide. It is to be noted that in the latter cycle we arbitrarily chose the temperature at which the carbon dioxide was to be condensed. This can be varied, with a resultant change in power requirement, but the calculations show that the minimum

power occurs at the limit where the ammonia carries the entire load.   On the other hand, the binary cycle has the practical advantages of avoiding pressures less than atmospheric, of requiring a smaller size of compressor, and of being readily adapted to producing refrigeration at two different temperature levels.

ABSORPTION REFRIGERATION

Absorption refrigeration was formerly used extensively for relatively low temperatures, but recent developments in the compression system have rendered the absorption process almost obsolete for industrial work, though it is still used even in some modern plants.   The equipment is
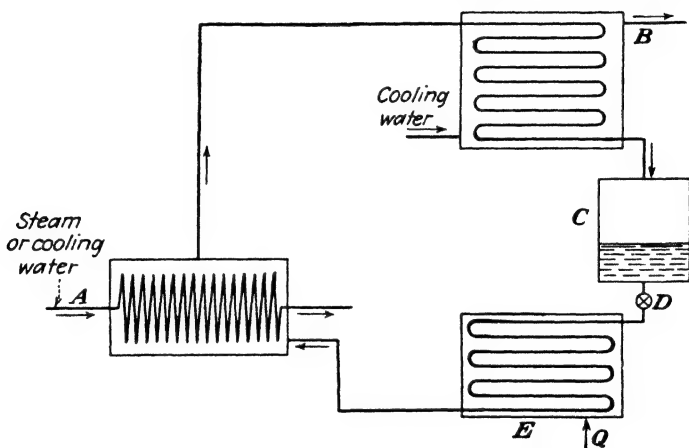
FIG. X.9.—Schematic diagram of an intermittent absorption system.

much bulkier than for the compression scheme, is less flexible, and requires more care and attention.   It does have the advantage of being able to operate with exhaust steam, and this may account for its continued life.   It is still important for small units such as household refrigerators. In spite of its relative unimportance in industry at the present time, it will be described briefly because of the interesting principles involved and because one can never be certain that some new development may not give it an entirely new impetus.

Intermittent Cycle.—In its simplest form, the absorption system requires no mechanical power and has no moving parts.   Its fundamental principle is illustrated in Fig. X.9.   The refrigeration is produced by evaporation of a liquid such as NH_3 or SO_2 just as in the compression process, but the pressure necessary for the liquefaction of the refrigerant is produced, not by mechanical power, but through the application of heat in a distillation process.   In the simple intermittent process shown

in Fig. X.9, vessel *A*, which acts alternately as a still and an absorber, takes the place of the compressor. In the distillation, or heating, phase of the cycle, the refrigerant is distilled from an absorbent in *A*, by application of steam or direct heat, at such a pressure that it will be condensed to a liquid when cooled by water in *B*. From the liquid receiver *C*, the refrigerant expands through the throttle *D* into the coils of the refrigerator *E*, where it evaporates, extracting heat. This refrigerating phase of the cycle occurs after the completion of the distillation phase, and the absorbent in *A* is now being cooled by water so that it will absorb the evaporated refrigerant. The absorbent may be either a liquid or a solid. The usual commercial system uses NH_3 and water, but solid absorbents such as silica gel or alkaline-earth chlorides have also been used.

The simplest practical application of this process was the Icyball household refrigerating unit shown in Fig. X.10. This consisted of the two containers *A* and *B*, joined by a tube. *A* acts intermittently as generator and absorber and *B* as condenser and refrigerator. The refrigerant is ammonia, and the absorbent is an ammonia-water solution. In the generation half of the cycle, *A* is heated by a burner and *B* is placed in a vessel of cold water. In the refrigerating part of the cycle, *B* is placed in the space to be cooled and *A* is exposed to the room temperature.
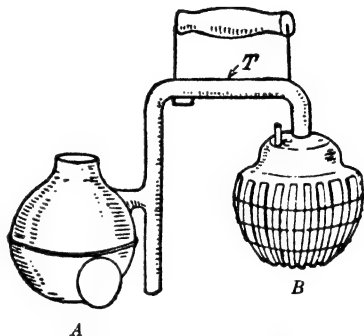
FIG. X.10.—Icyball refrigeration method. (*Courtesy of The Crosley Corporation, Cincinnati, O.*)

Continuous Processes.—A continuous-absorption system using ammonia as working fluid and water as absorbent is shown in Fig. X.11. The two functions of vessel *A* in the intermittent process have now been divided between a generator in which the ammonia is continuously distilled from a strong ammonia solution and an absorber in which the ammonia is continuously absorbed in a water-cooled weak ammonia solution. Since these two vessels are at different pressures and the ammonia solution must be transferred from the absorber to the generator, a pump is required. The system also contains a heat exchanger to transfer heat from the hot liquor leaving the generator to the cooled liquor from the absorber, and a so-called "analyzer," which is merely a short section of a rectifying column to remove most of the water vapor that distills over with the ammonia.

A thermodynamic analysis of this system can be made with the aid of data on the vapor pressure of ammonia-water solutions, on the composition

of the equilibrium vapor as a function of the temperature and composition of the liquid solution, and on the heats of solution.

Before leaving the subject of absorption refrigeration, mention should be made of the von Platen-Munters system used in the Servel Electrolux household units. This process is not used in industry, but the very clever application of a simple principle makes it of great interest, and other important applications of the principle might be developed.

This is a continuous-absorption system using ammonia and water. The need of a liquor pump has been circumvented in an ingenious manner.
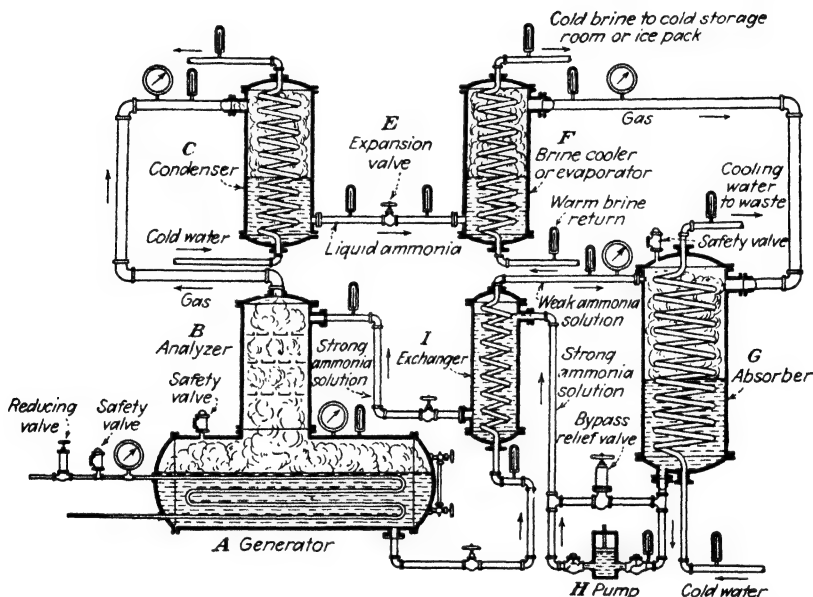
FIG. X.11.—Continuous ammonia absorption system. (*From John H. Perry, "Chemical Engineers' Handbook," p. 2541.*)

In the usual ammonia system the absorber and evaporator operate at one pressure level, about 30 lb. per sq. in., for example, and the generator and condenser at a much higher pressure—about 170 lb. In the von Platen-Munters process, however, the whole unit is at substantially the pressure of the condenser, and the necessary difference in pressure between the condensing NH_3 and the evaporating NH_3 is made up by the pressure of hydrogen gas. The NH_3 can still evaporate at low temperature even though the total pressure is 170 lb. per sq. in. because it evaporates into a stream of hydrogen, and the partial pressure of the NH_3 can be maintained below the desired 30 lb. Hydrogen circulates only between the absorber and the evaporator, where the low partial pressure of
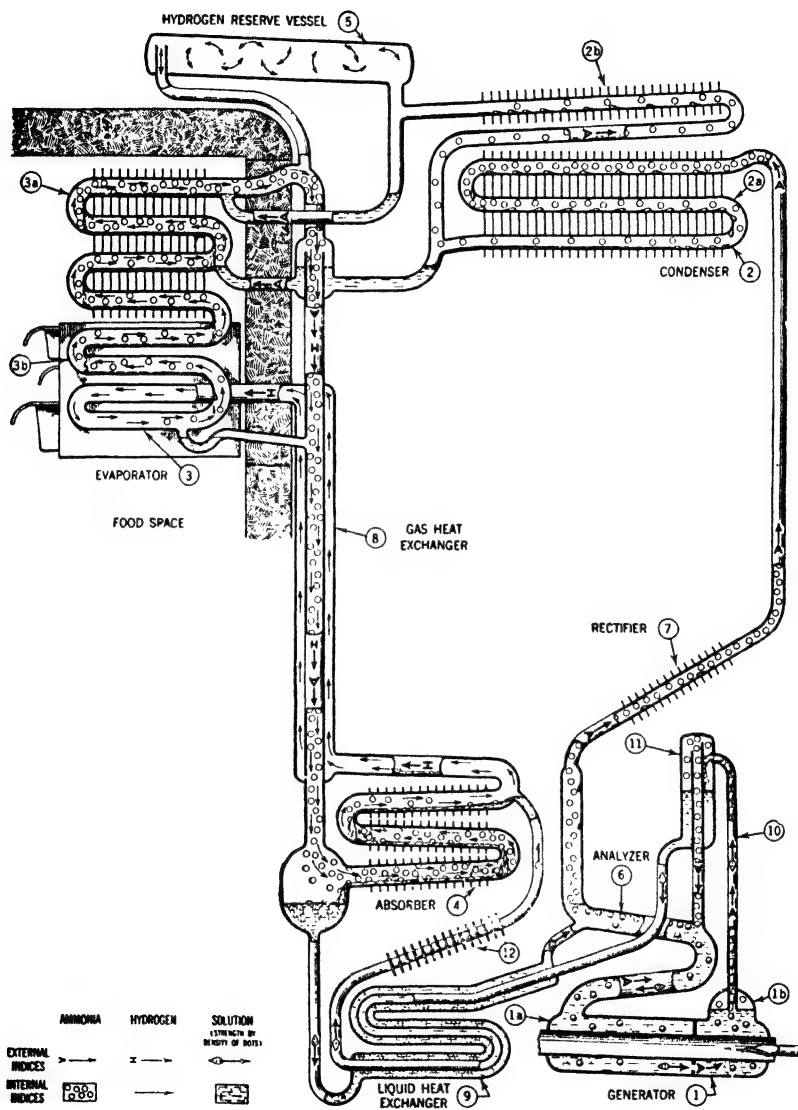
Fig. X.12.—Diagram of von Platen-Munters system used in the Servel Electrolux refrigerator.

NH_3 is to be maintained, and is prevented by liquid seals from getting into the generator or condenser, where the NH_3 vapor must be at the total pressure. The motive power for the system comes wholly from the heat of the gas flame in a manner to be described presently.

A diagram of the system is shown in Fig. X.12. Circulation of the liquor from generator (1) to absorber (4) and back again occurs by gravity, the necessary difference in level being created by the vapor-lift action of the boiling liquid in the generator, which carries liquid through pipe (10) to standpipe (11), from which it flows by gravity to the absorber and back to the generator. Circulation of hydrogen and NH_3 vapor between evaporators (3a) and (3b) and absorber (4) is accomplished by the difference in hydrostatic head between the H_2-NH_3 mixture in the inside tube of heat exchanger (8) and the much lighter hydrogen in the annulus. The vapors from the generator pass through an analyzer (6) and rectifier (7), whose function is to remove water vapor as in the ordinary absorption system. Ammonia vapor is condensed in the air-cooled condenser (2) and flows by gravity to the coils of the evaporator, where it meets a countercurrent stream of hydrogen from (8), which evaporates the ammonia at a temperature much lower than that corresponding to the total pressure in the system. The division of the condenser and evaporator into two sections is primarily for mechanical reasons and for the purpose of securing a closer control of conditions in the cabinet.

The NH_3-laden hydrogen enters absorber (4), where the NH_3 is absorbed in the countercurrent stream of weak liquor. The heat of absorption is removed by air flowing past the absorber fins. The hydrogen reserve vessel (5) acts as an automatic regulator to compensate for changes in the room temperature, which would otherwise seriously affect the operation of the system.

VACUUM REFRIGERATION

Refrigerating systems that operate at pressures well below atmospheric have become of considerable industrial importance within the past few years. They are particularly adapted to air conditioning, which is becoming of increasing importance in the process industries. There are two systems in common use, one having water vapor as the refrigerant and steam injectors for compression and the other making use of centrifugal compressors with either water vapor or organic vapors.

Water-vapor Refrigeration.—Systems using water vapor as the working fluid are among the oldest in the art of producing cold but have found little favor until recently. The early processes made use of the principles of both compression and absorption refrigeration, the latter generally

using sulphuric acid as the absorbent. The difficulty with a compression process using water vapor has been that a reciprocating compressor to handle the large volumes necessary for a system of any capacity would be entirely impracticable. The recent great development that has taken place in water-vapor refrigeration by the compression process has been due to the perfection of efficient steam-jet compressors.

The operating principle of the steam-jet vacuum system is simple, as may be seen from Fig. X.13. Water to be cooled is sprayed into the
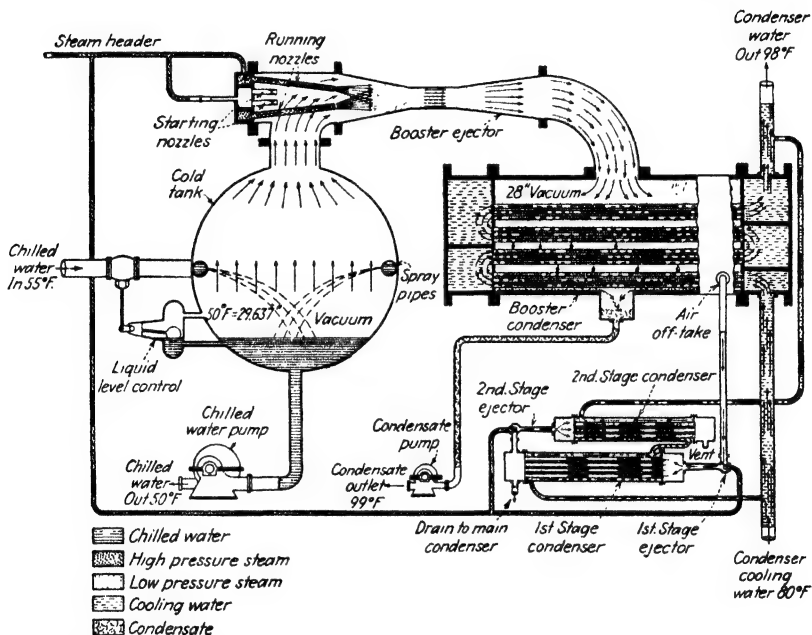
FIG. X.13.—Vacuum refrigeration system. (*Courtesy of Westinghouse Electric & Manufacturing Company.*)

cold tank, where it partly flashes to vapor, the remaining liquid being cooled to the saturation temperature corresponding to the pressure maintained in the evaporator. The low-pressure steam is compressed in the booster ejector by means of steam issuing from the nozzles in the ejector at very high velocities (of the order of 4,000 ft. per sec.). It is necessary to compress the vapor, not up to the atmospheric pressure, but only to such a pressure that it can be condensed by cooling water, as shown in Fig. X.13. From the condenser, which may be either of the indirect-contact (surface) type or the jet (direct-contact) type, the condensate is removed by a pump. The noncondensable gases, which are always present as a result of small leaks or as dissolved gases in cooling

water, are removed by a vacuum pump operating between the pressure in the condenser and that of the atmosphere. This may be the usual type of mechanical pump, or it may be another steam ejector.

The conditions of operation of such a system may be made clearer by a numerical example.

Illustration 8.—One hundred tons of refrigeration is to be produced by a water-vapor system. The chilled water is to be at 40°F. and will be allowed to rise to 55°F. in the process of extracting heat. Cooling water is at 80°F. and will be assumed to rise to 100°F. in the condenser. Calculate (1) pressure in the evaporator, (2) pressure in the condenser, (3) amount of chilled water to be circulated, (4) amount of make-up water, and (5) volume of vapor to be compressed. Assume ideal operation.

1. The pressure in the evaporator will be the vapor pressure of water at 40°F., which, from steam tables, is 0.1217 lb. per sq. in. abs., or 0.248 in. Hg.

2. The condenser pressure will be the vapor pressure at 100°F., or 0.949 lb. per sq. in.

In both these cases minor effects such as presence of noncondensable gas and pressure drop due to flow have been neglected.

3. Pounds of water per minute = $(200 \times 100)/(55 - 40)$ = 1,332.

4. The flash evaporation of the water is a process at constant enthalpy.

For water at 55°F., H = 23.07 B.t.u. per lb.

At 40°F., H = 8.05.

H of saturated vapor at 40°F. = 1,079.3

Then, for constant H, $23.1 = 1,079.3x + 8.05(1 - x)$

where x = fraction of the water vaporized.

$$x = 0.0138$$

Lb. of make-up water = $0.0138 \times 1,332$ lb./min. = 18.4 lb./min.

5. Assuming ideal gas,

$$\text{Volume (cu. ft./min)} = \frac{359 \times 500 \times 14.7 \times 18.4}{492 \times 0.1217 \times 18.0} = 45,000$$

From this last figure it is clear that reciprocating compressors would be entirely out of the question.

Further calculations can be made to show that the capacity of such a system varies greatly with the temperature of the chilled water. The great advantage of this process lies in its simplicity. There are no moving parts other than liquid pumps, and no special fluids are required. It is mainly adapted to producing refrigeration to a limit of about 35°F. Lower temperatures might be produced by using salt solutions, but this has not been put into practice.

Steam consumption to produce a ton of refrigeration varies widely with the conditions, the chief variables being the steam pressure, the volume and temperature of the cooling water, and the refrigerated water temperature. D. H. Jackson[1] gives actual test data on steam consumption as a function of the four variables mentioned above, for saturated

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[1] JACKSON, D. H., *Ind. Eng. Chem.*, **28**, 522–526 (1936).

steam at 100 lb. gauge, a pressure commonly used in practice. The steam requirement increases rapidly as the pressure is lowered. It may be estimated fairly closely by the method illustrated in Chap. VII on pages 290 to 293. It was there shown that, for steam at 100 lb. per sq. in. absolute pressure, 40°F. refrigeration temperature, and condensation at 101.7°F. (1 lb. per sq. in.), 2.5 lb. of motive steam was required per pound of evaporated water. Assuming that condensate at 90°F. is used as make-up water, then

Net refrigerating effect per pound of water evaporated
= enthalpy of saturated steam at 40°F. − enthalpy of water at 90°F.
$$= 1,021 \text{ B.t.u.}$$

(This may readily be seen by an energy balance on the system, including the cold tank and the circulating chilled water.)

Lb. steam per hr. per ton of refrigeration $= 2.5 \times \dfrac{12,000}{1,021} = 29.4$

This amount of steam used to drive either a reciprocating or a centrifugal compressor would produce more refrigeration because the steam-jet compressor is relatively inefficient, but it has other advantages that more than offset the lower economy in many cases.

It is not essential to use high-pressure steam. Exhaust steam at substantially atmospheric pressure can be used, but the quantity required is greater, as may readily be shown by calculation.

Centrifugal-compression System.—This may be a system which uses water vapor as the refrigerant but in which a centrifugal compressor replaces the steam-jet booster. The characteristics of centrifugal compressors have already been discussed in Chap. VII. It was shown there that they are adapted to the handling of large volumes at low or moderate pressures. In fact, it may be stated that large volumes are essential to the successful use of such compressors. The pressure developed in any stage is approximately proportional to the square of the diameter of the rotor at a given speed of revolution, and hence a small machine would require an excessive number of stages. Since the pressure increment in one stage of centrifugal compression depends directly on the density of the gas being compressed, there is an advantage in using vapors of higher density than water vapor. Dichloromethane (CH_2Cl_2), dichloroethylene ($C_2H_2Cl_2$), and Freon-11 (CCl_3F) are some of the fluids that have been used in place of water vapor in vacuum systems.

Dichloroethylene has approximately five times the density of water vapor at the same temperature and pressure, and therefore a given centrifugal compressor would require five times as many stages to compress over a given pressure range with water vapor as with dichloro-

ethylene vapor.   Actually, of course, one is interested in a given tempera-
ture range, and the pressures will be quite different for different
refrigerants, so that it is better to deal with pressure ratio.   It can readily
be shown from the fundamentals of centrifugal compression that the pres-
sure ratio increases with the molecular weight of the vapor, regardless
of the absolute pressure.   Furthermore, the pressure ratio for a given
temperature range is less for most organic vapors than for water.   For
example, for a 40 to 100°F. temperature range, the pressure ratio is
7.8 for water and only 3.9 for CH_2Cl_2.   The net result of both these
factors is that a simpler compressor can be used for centrifugal refrigera-
tion with an organic vapor than when water vapor is used.

The centrifugal compressor has a higher first cost than a steam
ejector, but the latter will probably require somewhat more steam per ton
and will place a greater load on the condenser, necessitating a larger
condenser and more cooling water.   Both these vacuum processes are
able economically to handle a fluctuating load, such as is common in air
conditioning, better than the ordinary compression process.

SOLID CARBON DIOXIDE PROCESSES

One important application of refrigeration cycles is in the manu-
facture of solid CO_2.   A brief excursion into this field is desirable since
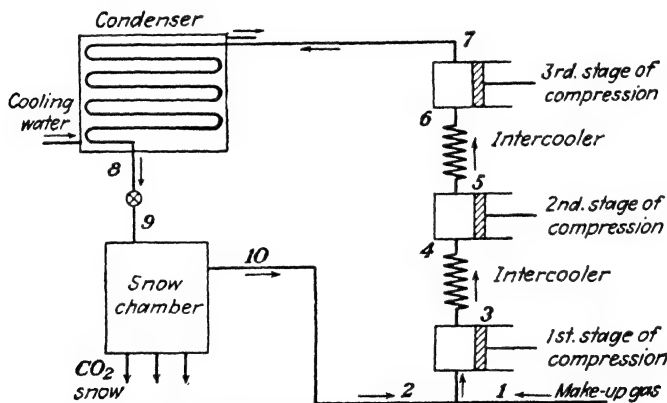
Fig. X.14.—Simple solid carbon dioxide system.

a study of various processes for this purpose affords many interesting
applications of thermodynamic principles.

A very simple carbon dioxide process is shown schematically in
Fig. X.14.   Pure CO_2 at atmospheric pressure and temperature mixes
with return gas from the snow chamber, and the mixture enters the first
stage of a three-stage compressor, in which it is compressed to a suffi-

ciently high pressure to permit liquefaction of the CO_2 in the water-cooled condenser (the high pressure required to condense CO_2 with ordinary cooling water necessitates the use of at least three stages of compression). The liquid CO_2 expands through a throttle into the snow chamber at atmospheric pressure, where solid that has been formed is separated from the gas, the latter being recycled.

The analysis of this cycle to determine the yield of solid and the power requirement, as a function of the important variables, is most readily accomplished with the aid of a *TS* diagram. For this purpose, use will be made of the diagram of the Liquid Carbonic Corporation given in the Appendix. In Fig. X.15 the cycle is represented on an
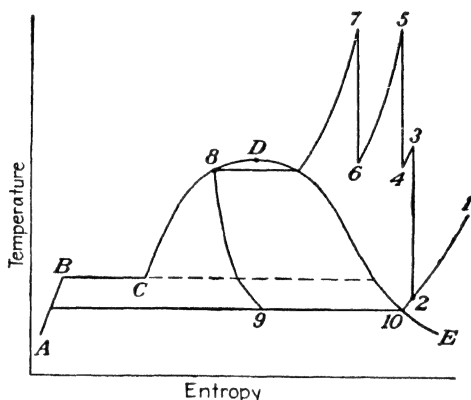
Fig. X.15.—Simple carbon dioxide cycle represented on a temperature-entropy diagram.

outline of such a diagram. *AB* gives the entropy of saturated solid in equilibrium with vapor; *BC* is the entropy change from solid to liquid, both in equilibrium with vapor. This change occurs at the triple point, for which the temperature is $-69.6°F$. and the pressure 75 lb. per sq. in. *CD* is the saturated-liquid line, and *DE* that of saturated vapor, the critical point *D* being at $88°F$. and 1,070 lb. per sq. in. abs. The numbers on the diagram correspond with the numbers in Fig. X.14 in that they refer to the same points in the cycle.

Illustration 9.—Estimate the theoretical power requirement per ton of solid CO_2 for the cycle shown in Figs. X.14 and X.15.

The analysis of the cycle will be based on the following main assumptions:

1. Make-up gas is pure CO_2 at $70°F$. and 1 atm. absolute pressure.

2. Compression is isentropic.

3. Perfect intercooling between stages.

4. Intermediate pressures between stages chosen so that same work is done in all stages.

5. Equilibrium between phases in condenser and snow chamber.

6. No heat leak.

7. Negligible pressure drop due to fluid flow except at expansion valve.

8. Cooling water at 70°F.

9. 10°F. minimum terminal temperature difference in heat exchangers.

We shall start with the liquid CO_2 at point 8 and calculate the yield of snow per pound of liquid CO_2 expanded. Assuming that the condensed liquid is not sub-cooled, $t_8 = 80°F.$, on the saturated-liquid line. Following a constant-enthalpy line to 1 atm. (8-9), the quality is found to be 0.765, or 23.5 per cent of the liquid CO_2 is obtained as solid. The residual vapor, represented at point 10, mixes at constant pressure with the make-up gas (1), and the resultant mixture (2) goes to the compressor. The condition of the mixture is found from the heat-balance equation

$$0.765(H_2 - H_{10}) = 0.235(H_1 - H_2)$$
$$H_{10} = 275.5, \qquad H_1 = 312$$
$$\therefore H_2 = 283.7 \quad \text{and} \quad t_2 = -74°F.$$

The determination of the conditions of compression is a matter of trial and error to equalize the quantities of work in the three stages. The following table gives conditions which meet this criterion with sufficient exactness:

Item	1st stage	2d stage	3d stage
Suction temp., °F	−74	80	80
Discharge temp., °F	100	240	232
Suction pressure, lb./sq. in	14.7	75	265
Discharge pressure, lb./sq. in	75	265	970
Pressure ratio	5.1	3.53	3.66
Enthalpy at suction, B.t.u./lb	283.7	312	306
Enthalpy at discharge, B.t.u./lb	316.5	345	340
ΔH or work	32.8	33	34

$$\text{Total work of compression} = 100 \text{ B.t.u./lb.} = \frac{100 \times 2,000}{0.235 \times 2,545 \times 1.34}$$
$$= 250 \text{ kw.-hr./ton solid } CO_2$$

The lines 2-3-4-5-6-7 in Fig. X.15 represent the compression process and 7-8 the cooling and liquefaction of the CO_2.

Since solid CO_2 must be produced at a cost of not over 1.0–1.5 cents per pound, it is evident that energy (or steam if steam-driven compressors are used) is an important item, hence, it is desirable to consider any changes in the cycle that would lead to a higher yield per unit of energy expended. One possibility is to utilize the cold gas from the snow chamber to subcool the liquid CO_2 as indicated in Fig. X.16.

Applying the first law to the heat exchanger,

$$H_8 - H_9 = x(H_{12} - H_{11})$$

where x is the quality of the expanded mixture at point 10. Allowing a 10°F. temperature difference at the warm end of the exchanger, H_{12} is then fixed. This leaves x and H_9 as unknowns, and another equation

is required. It is obtained from an enthalpy balance on the snow chamber:

$$H_9 = xH_{11} + (1 - x)H_{13}$$

Solving simultaneous equations,

$$x = \frac{H_8 - H_{13}}{H_{12} - H_{13}} = \frac{217 - 30.5}{312 - 30.5} = 0.663$$

Since the compressor intake is now 70°F. instead of −74°F., the work will be increased to 114 B.t.u. per lb.; but the yield is so much greater that the work per ton of solid has been decreased to 198 kw.-hr. A dis-
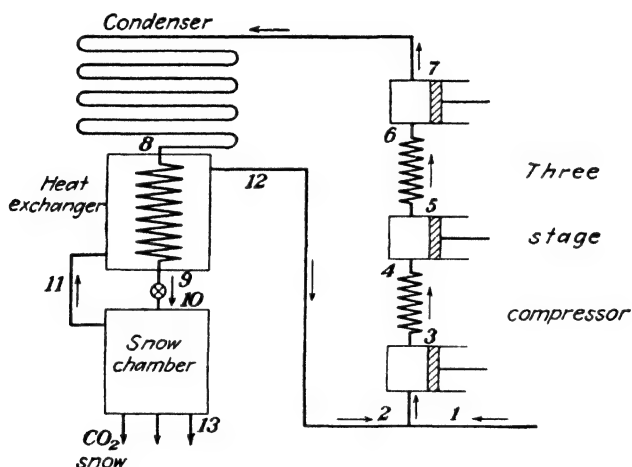
Fig. X.16.—Solid-carbon dioxide cycle in which cold expanded gas is used to subcool the liquid.

advantage is that the compressor displacement has been increased about 1.37 times.

Other possibilities for reduction of energy requirement include stage expansion of the liquid with each vapor going to the appropriate stage of the compressor and also the use of a binary NH_3-CO_2 cycle. Various combinations may also be used. The analysis of any proposed variation of the simple cycle can be made by the methods previously illustrated. [For further details on the thermodynamics of solid CO_2 cycles a paper by A. B. Stickney may be consulted, *Refrigerating Eng.*, **24,** 334–342 (1932).]

The minimum possible amount of energy to produce a pound of solid CO_2 from CO_2 gas at 1 atm. and 70°F., assuming that heat can be rejected at 70°F., is given by Eq. (X.11). From the *TS* chart,

$$\Delta H = 281.5$$
$$\Delta S = 0.787$$
$$\therefore W \text{ (per ton)} = 2{,}000(530 \times 0.787 - 281.5) = 271{,}000 \text{ B.t.u.}$$
$$= \frac{271{,}000}{3{,}415} \text{ kw.-hr.} = 79.4$$

The best cycle analyzed by Stickney, which was the binary fluid cycle using ammonia to condense the CO_2, had an ideal energy consumption about 1.4 times this minimum. Therefore its efficiency may be said to be 72 per cent, based on the Carnot cycle.

It is of interest to note that if the snow chamber is kept just above 75 lb. abs. (the triple point) the expansion will yield a mixture of liquid and solid which is more readily compacted to a dense cake than is the snow. After the requisite amount of mixture has been formed, the pressure is then lowered to 1 atm. to convert the liquid to solid. This is the basis of one important process for CO_2 manufacture.

THE REFRIGERATION CYCLE AS A HEATING METHOD

Lord Kelvin in 1852 proposed the use of the refrigeration cycle as a means of heating buildings, and this general scheme has commonly been referred to as the "Kelvin warming engine." Although simple in principle and apparently very attractive from an energy-consumption standpoint, no practical application was made of it until quite recently. Several installations have now been made, and the results are reasonably satisfactory. Purely as a method of heating it is doubtful if it can justify itself economically, but it may offer considerable promise as a combination scheme for heating in winter and air conditioning in the summer.

For an ideal Carnot heat-engine or refrigeration cycle, we have the equation

$$W = Q_1 - Q_2 = Q_1 \frac{T_1 - T_2}{T_1} \tag{X.29}$$

If $T_1 = 530°R.$ (70°F.) and $T_2 = 492°R.$ (32°F.),

$$\frac{Q_1}{W} = \frac{530}{70 - 32} = 13.9$$

Thus an expenditure of 1 B.t.u. in the form of work should, in an ideal system, make it possible to supply nearly 14 B.t.u. of heat at 70°F. when the outside temperature is 32°F. This would appear to offer an economical means of utilizing electrical energy for house or building heating. Electrical energy used irreversibly, as in a resistance, to produce heat could yield only an equivalent amount, but when used to operate a heat pump the heat released at the upper temperature level may

be many times that equivalent to the electrical energy supplied, as Eq. (X.29) shows. However, it should also be borne in mind that in the generation of electrical energy from coal a large proportion of the chemical energy has been made unavailable and the electrical energy obtained, at the very best, is only about 25 per cent of the energy given out as heat in the combustion of the coal. Thus any system of heating by electrical energy starts with this initial handicap as compared with the direct use of fuel. On the other hand, one should not lose sight of the fact that fuel can be burned much more efficiently in a large central station than in the usual small heating plant.

There are many practical difficulties that militate against the commercial development of this interesting idea. In the first place, because of the unavoidable irreversible effects of friction in any practical refrigeration system and because of the necessary temperature differences for heat transfer, the coefficient of performance Q_1/W will be much less than the ideal. A fair average figure for the efficiency of a compression-refrigerating system when used as a heating plant, referred to the Carnot cycle between the same temperature levels, is about 60 per cent.[1] For an outdoor temperature of 32°F. and an inside temperature of 70°F., it might be assumed that refrigeration and condensing temperatures are 20°F. and 100°F., respectively. On this basis, *i.e.*, with the above efficiency and Δt's, the coefficient of performance would be only 4.2 instead of 13.9. In severe weather with an outside temperature of 0°F. and an assumed refrigeration temperature of $-15°$F., the practical coefficient of performance is 2.9.

Another difficulty arises from the fact that as the outside temperature varies the system reacts in just the opposite way from that desired. Thus as the refrigeration temperature (that at which heat is absorbed) is lowered, the capacity of the usual compression-refrigeration system is rapidly reduced, and therefore much less heat would be supplied when more is needed. If the system is designed to take care of the most severe condition, it will be much larger and less economical than necessary for the average condition. One method of meeting this difficulty is to extract the low-temperature heat from a uniform-temperature source such as water from a deep well. Another scheme is to store heat in water during mild weather and then in severe weather to use this stored heat both to take up some of the heating load and to act as a heat source.

The first practical application of the Kelvin warming engine appears to have been made by an electrical engineer, T. G. N. Haldane,[2] who

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[1] This means that the practical coefficient of performance is 60 per cent of the ideal one.

[2] HALDANE, T. G. N., *J. Inst. Elec. Eng.*, **68**, 666–675 (1930).

describes an installation in his own house that has operated satisfactorily. This was essentially an ordinary ammonia refrigerating system with the condenser acting as a heater for hot water to the radiators. With an evaporation temperature of 20°F. and condensing temperature of 100°F., a coefficient of performance of 2.5 was realized. P. Sporn and D. W. McLenegan[1] describe in detail an installation in a small office building in Salem, N. J., that was successfully operated as a heating plant in winter and an air-conditioning system in summer. The heat source in this case was deep-well water that was substantially constant in temperature at 56°F. An average coefficient of performance of 3.9 was obtained (this does not include the work of the water pump, which would lower it to 3.5).

An installation of considerable size was made in the Edison Building, Los Angeles, Calif. This uses methyl chloride and provides 480 tons of refrigeration for air conditioning in the summer and 60,000 B.t.u. per min. for heating in winter. Heat is absorbed from water that cools from 40 to 35°F., the water being reheated by direct contact with air in a forced-draft tower. The heating of the building is by air, which in turn is heated by the water from the methyl chloride condenser. A coefficient of performance of about 2.3 was expected. Actual tests showed coefficients varying from 1.45 to 1.98, based on total power input to the compressors and all auxiliaries. In the test that gave the coefficient 1.98, the outdoor temperature was 48°F. and the air was heated to 74.5°F., so that the theoretical coefficient of performance is 20. This would appear to indicate considerable room for improvement.

The most recent application that has come to the author's attention is that in the building of the United Illuminating Company in New Haven, Conn. This installation is described in a paper by Lawless,[2] but no performance data have been presented. It is a combined heating and air-conditioning system with well water at a constant temperature of 55°F. as the heat source for the winter heating cycle. The reversed refrigeration heating system was designed for a minimum outside temperature of 20°F.; when the temperature falls below this, additional heat is provided from a hot-water storage system. The water in this system is heated by direct conversion of off-peak electrical energy.

LOW-TEMPERATURE PROCESSES

Processes for the liquefaction and subsequent separation of gases are of increasing importance in industry. The manufacture of oxygen,

[1] SPORN, P., and D. W. McLENEGAN, *Heating, Piping and Air Conditioning*, **7**, 402–409 (1935).
[2] LAWLESS, A. J., *Heating, Piping and Air Conditioning*, August and September, 1940.

nitrogen, and argon from the air by low-temperature methods is old and well established; but the future possibilities for increased utilization of oxygen or oxygen-enriched air are so great that continued activity in this field is stimulated by the desire for cheaper and more reliable methods of separation. The production of hydrogen by low-temperature methods from water gas and coke-oven gas is well known abroad but has been practiced only to a limited extent in this country. A distinctly American achievement in this field is the production of helium from natural gases. A very recent development, also American, is the liquefaction and storage of natural gas as a means of taking care of peak demands in the wintertime. From these few examples it is evident that the field of low temperatures is of such industrial importance that it deserves more space than can be devoted to it in this book. We must content ourselves with only a brief excursion into this interesting field.

Methods of Producing Low Temperatures.—For our present purpose low temperatures will be arbitrarily defined as temperatures below 200°K. ($-100°$F.). The same general principles apply to refrigeration in this region as in that already treated, but there are some important differences in detail. There are just three general methods that have been applied in engineering practice for producing refrigeration at or below this level; these are

1. Vaporization of a liquid.
2. The Joule-Thomson effect.
3. Expansion in an engine doing external work.

Actual processes may utilize only one of these methods or combinations of them. Let us now consider each one separately in a little more detail.

It is evident from the properties of liquids that method 1 cannot be used over a very wide temperature span if only one liquid is used. The maximum possible range would be from the critical point down to the triple point, and in most cases the triple-point pressure is so low that it becomes impracticable to realize the whole of this range. The lowest temperature that it is feasible to produce with a single fluid by this method (*i.e.*, the vapor-compression process already discussed) is about $-100°$F. However, by using two or more fluids in series such that the one of lowest boiling point is condensed through the refrigerating effect caused by evaporation of the one next higher in boiling point, and so on, until the one of highest boiling point is condensed by the atmosphere or by cooling water, much lower temperatures can be reached. Such a system is known as a "cascade." One that has been used for liquefaction of air utilizes the three fluids ammonia, ethylene, and methane. There is a lower limit to the temperature attainable by such a method, set by the fact that the critical temperature of the lowest usable fluid must be higher than the triple-point temperature of the next higher one. Refer-

ence to Table X.2 shows that 63°K. is this lower limit since it is the lowest temperature which could be produced by evaporating liquid nitrogen and the next fluid, neon, has a critical point so low that it could not be condensed to a liquid by the boiling nitrogen.

Method 2 can be used to produce temperatures to within a few degrees of absolute zero. This may seem astonishing at first thought because as was shown in Chap. VII the lowering of temperature produced by a Joule-Thomson expansion even from high pressures is quite small, and

TABLE X.2.—DATA ON SOME FLUIDS USED IN REFRIGERATION

Fluid	Normal boiling point, °K.	Triple point		Critical point	
		Temp., °K.	Pressure, atm.	Temp., °K.	Pressure, atm.
He..............	4 4	....	......	5.4	2.26
H₂..............	20.4	14.1	0.071	33.3	12.80
Ne..............	27 3	24 5	0.425	44.5	26.86
N₂..............	77.4	63.3	0.127	126.1	33.49
A...............	87 0	84.0	0.673	150.8	48.0
O₂.............	90 2	54 8	0 0026	154.4	49.71
CH₄.....	111 8	90 0	0.092	190.3	45.60
Krypton......	121	104	..	210.6	54.2
C₂H₄....	169.5	104	.....	282.7	50.65
N₂O..	183 4	170.9	....	309.7	71.65
C₂H₆....	184	101		306.0	48.4
CO₂......	195	216.5		304	72.8
Propane......	231	83.3	.	370	42
NH₃..............	240	195	....	406	112.5
Freon-12.......	243	118	...	384	39.6
Methyl chloride.....	249.1	170.3	.. .	416	65.9
Isobutane.....	261	....	. ..	407	30.2

starting with air at room temperature one could only lower the temperature about 50°C at best. However, by combining the expansion with heat exchange as shown in Fig. X.17, the small cooling effect can be made accumulative. High-pressure gas at room temperature enters the low-temperature system at (1); when the whole system is at the temperature of the surroundings, the gas arrives at (4) still at room temperature, drops in temperature when expanded, and is then recirculated through the exchanger counter to the incoming high-pressure gas. This cools the high-pressure gas so that it arrives at (4) somewhat colder and becomes still colder after expansion to (5). Obviously, the temperature at (5) will continue to fall until some compensating effect takes place; neglecting heat leakage from the surroundings into the system for the

moment, this can only be a partial liquefaction at (5), followed by separation of the two phases. Since only a part of the fluid returns through the exchanger, the refrigeration available for cooling the high-pressure gas is diminished and eventually a steady state is reached that is characterized by an energy balance.

There is also a limitation on this method of producing refrigeration, and this is that the initial state of the fluid must be such that its isothermal enthalpy change on expansion is an increase. This condition is satisfied by all fluids at room temperature except hydrogen and helium. As would be expected from the theorem of corresponding states, even these two gases can be liquefied by the Joule-Thomson effect if the initial temperature is maintained at some lower level (about 100°K. for hydrogen and 20°K. for helium) by an external refrigeration system.

The use of method 3 has already been referred to in connection with refrigeration at higher temperature levels. Its use at low temperatures has been retarded by the mechanical difficulties involved in maintaining proper functioning of reciprocating engines at temperatures at which no liquid lubricant is possible. The problem was originally solved by Claude, who developed a special leather packing that remained pliable at liquid-air temperatures. Later investigators used other ingenious ways of overcoming this difficulty, such as Micarta piston rings, a plunger-type expander of small clearances, and the use of a close-fitting piston with gas-filled grooves acting as piston rings to prevent contact between piston and cylinder. By such an expander as the last mentioned, Kapitza[1] has succeeded in liquefying helium without the necessity of using a hydrogen-liquefying cycle to precool. Later, the same investigator[2] overcame the lubrication difficulty and gained other advantages by the use of a turbine expander.

Fig. X.17.—Use of Joule-Thomson effect for low-temperature refrigeration.

It should be noted that even an isentropic expansion (as distinct from an isenthalpic one) would not by itself be a feasible means of continuously liquefying a gas such as air. A practical process combines the expansion with heat exchange to make the refrigeration accumulative, just as in the case of method 2.

[1] Kapitza, P., *Proc. Roy. Soc.*, **A147**, 189 (1934).

[2] Kapitza, P., *J. Phys.* (*U S.S.R.*), **1**, 7–28 (1939).

Minimum Work of Liquefaction or Gas Separation.—It is clear from first principles that the change in state involved in the liquefaction of a gas or the separation of a gas mixture entails a decrease in entropy. Since the entropy of an isolated system never spontaneously decreases, work must be done to accomplish it, and there will be at the same time a transfer of heat to the surroundings. Thus we may represent the steady-state process of liquefaction or separation (as far as net energy effects are concerned) by the simple diagram of Fig. X.18. The entire apparatus (with one exception to be noted) for carrying out the process is located inside a box indicated by the rectangle; its details are immaterial

H_1 = Total enthalpy of fluid entering
H_2 = Total enthalpy of fluid leaving
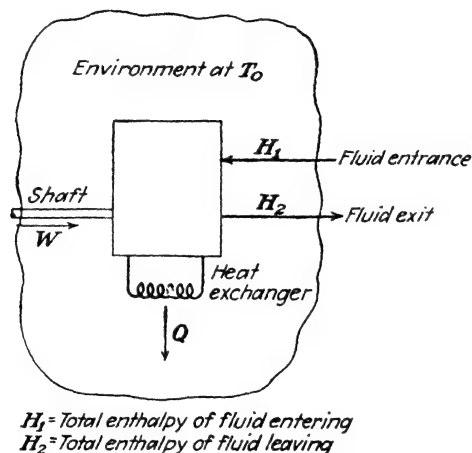
Fɪɢ. X.18.—Energy balance of a continuous liquefaction, or gas-separation, process.

to the present argument. There enters the box a shaft for doing work and two (or more) pipes for conveying fluids in and out. The box is placed in an environment at constant temperature T_0, and the only connection between the apparatus inside the box and the environment is the heat exchanger. From the first law we have

$$-W = \Delta H - Q \qquad (X.30)$$

From the second law, $\Delta S = \Delta S_e$

$$= \frac{Q}{T_0} \qquad (X.31)$$

if the process is reversible, and

$$\Delta S < \Delta S_e = \frac{Q}{T_0} \qquad (X.32)$$

if the process is irreversible, where ΔS is the entropy change (a decrease)

of the fluid and ΔS_s that of the environment (an increase). Substituting Eq. (X.31) in Eq. (X.30)

$$-W = \Delta H - T_0 \Delta S \qquad (X.33)*$$

The minimum work of the process, given by Eq. (X.33), is entirely independent of the actual mechanism and depends only on the properties of the fluid.

Illustration 10.—What is the minimum work necessary (1) to liquefy nitrogen initially at 80°F. (300°K.) and 1 atm., to produce liquid nitrogen at 1 atm., and (2) to separate air into liquid oxygen and gaseous nitrogen both at 1 atm. and the nitrogen at 80°F.? Express the results in horsepower-hours per pound.

The following values of H and S are taken from the paper of Millar and Sullivan[1] except as otherwise noted:

$$H \text{ of } N_2 \text{ at } 80°F. \text{ and } 1 \text{ atm.} = 2,884$$
$$H \text{ of liquid } N_2 \text{ at the normal boiling point} = 0$$
$$S \text{ of } N_2 \text{ at } 80°F. \text{ and } 1 \text{ atm.} = 26.70$$
$$S \text{ of liquid } N_2 \text{ at } 80°F. \text{ and } 1 \text{ atm.} = 0$$
$$H \text{ of air at } 80°F. \text{ and } 1 \text{ atm.} = 2,963$$
$$S \text{ of air at } 80°F. \text{ and } 1 \text{ atm.} = 28.08$$
$$H \text{ of } O_2 \text{ at } 80°F. \text{ and } 1 \text{ atm.} = 3,251$$
$$S \text{ of } O_2 \text{ at } 80°F. \text{ and } 1 \text{ atm.} = 28.41$$
$$H \text{ of liquid } O_2 \text{ at the normal boiling point} = 158$$
$$S \text{ of liquid } O_2 \text{ at the normal boiling point} = 1.90$$

The units are centigrade heat units, pound-moles, and degrees Kelvin. The enthalpy of air was calculated from that of O_2 and N_2 by assuming no heat of mixing (ideal solution).

Thus, $\quad H_{air} = 0.790 H_{N_2} + 0.210 H_{O_2}$
$$= 0.790 \times 2,884 + 0.210 \times 3,251 = 2,963$$

The entropy of air was calculated by Eq. (IV.53) (ideal gases assumed).

$S_{air} = 0.790 \times 26.70 + 0.210 \times 28.41 - 1.987(0.790 \ln 0.790 + 0.210 \ln 0.210)$
$\quad = 28.08$

(1) $\qquad W = (2,884 - 0) - 300(26.70 - 0)$
$$= -5,136 \text{ c.h.u./lb.-mole}$$
$$= \frac{-5,136}{28 \times 1,413} \text{ hp.-hr./lb.} = -0.130$$

(2) $\quad W = 2,963 - 0.79 \times 2,884 - 0.21 \times 158$
$$- 300(28.08 - 0.79 \times 26.70 - 0.21 \times 1.90) = -1,324 \text{ c.h.u./lb.-mole}$$
$$= 0.0323 \text{ hp.-hr./lb. of air}$$
$$= 0.139 \text{ hp.-hr./lb. of } O_2$$

Owing to various irreversible effects actual processes will require more work than the minima obtained in this illustration, and the ratio

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* This equation is, of course, the same as Eq. (X.11), and the derivations are essentially the same. The justification for this apparent repetition is that experience shows it to be desirable in the teaching of thermodynamics to present the same argument from different points of view.

[1] MILLAR, R. W., and J. D. SULLIVAN, Thermodynamic Properties of Oxygen and Nitrogen, *U.S. Bur. Mines Tech. Paper* **424** (1928).

of the minimum reversible work to the practical work of an operating process will be known as the "thermodynamic efficiency." Two other efficiencies have been found to be useful and are defined as follows:

$$\text{Cycle efficiency} = \frac{\text{reversible work}}{\text{theoretical work for ideal operation of the cycle}}$$

$$\text{Practical efficiency} = \frac{\text{theoretical work for ideal operation of the cycle}}{\text{practical work for the cycle}}$$

Obviously, the product of the latter two efficiencies equals the thermodynamic efficiency. Ideal operation of a cycle means that there are no irreversible effects except those inherent in the particular cycle. The irreversible effects commonly encountered in a low-temperature cycle are (1) heat leak from the surroundings, (2) heat transfer in exchangers under finite Δt, (3) fluid friction in piping and equipment, (4) mechanical friction in engines, (5) throttling expansion, and (6) material transfer between phases not at equilibrium. Heat leak can always be considered as reduced to zero at the limit, and the same is true of mechanical friction; but a throttle expansion may be inherent in the particular cycle. Likewise, some temperature differences are inherent in a particular situation, and others can be reduced to zero as a limit (see Chap. IX).

It can be taken as a rule without exception that whenever an irreversible process occurs in any part of a low-temperature process it must inevitably be compensated by a certain amount of work done. This is a very useful guiding principle to have well in mind in comparing various low-temperature processes.

Liquefaction of Gases by Joule-Thomson Effect (Linde Process[1]).— The essential elements of such a process have already been depicted in Fig. X.17. When the process has reached a steady state, application of the first law leads to the equation

$$H_1 + q_L = \zeta H_2 + (1 - \zeta)H_3 \qquad (X.34)$$

or
$$\zeta = \frac{H_3 - H_1 - q_L}{H_3 - H_2} \qquad (X.35)$$

where H_1, H_2, etc. = the enthalpies of the fluid at the numbered points on the diagram.

ζ = fraction of entering gas that is withdrawn as liquid.

q_L = quantity of heat leaking into the apparatus from the surroundings per unit of entering gas.

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[1] The German engineer Carl von Linde was the first to apply this method to the commercial production of oxygen and nitrogen from the air.

It is of interest to note that the degree of liquefaction is determined by the enthalpy difference at the warm end of the exchanger and not by conditions at the point where the actual expansion takes place.

With this simple equation and a table of properties one can easily estimate the fraction of any gas that will be liquefied and how this fraction depends on the pressure, temperature, heat leak, exchanger efficiency, and other factors. The following will illustrate the method.

Illustration 11.—Air is to be liquefied by a simple Linde process. Assume that air enters the low-temperature system at 80°F. and 100-atm. pressure and expands to 1-atm. abs. The rate of air flow is 50 cu. ft. per min. at 60°F. and 1 atm. The following is required:

1. Compute fraction of air liquefied, pounds of liquid produced per hour, and cycle efficiency. Assume ideal operation, *i.e.*, no heat leak, zero temperature difference at the warm end of the exchanger,[1] and reversible adiabatic compression.

2. Estimate per cent decrease in production if heat leak is 35 B.t.u. per lb.-mole of air entering and a temperature approach of 5°C. is obtained at the warm end of the exchanger.

3. Estimate per cent increase in production over case 1 if the pressure is 200 atm.

(1) From a TS diagram[2] for air, one obtains the values

$$H_1 = 120.5, \qquad H_2 = -53, \qquad H_3 = 129.7 \qquad (B.t.u./lb.)$$

Substituting in Eq. (X.35), $\zeta = 0.050$

$$50 \text{ cu. ft./min.} = \frac{50 \times 492 \times 60 \times 29}{359 \times 520} \text{ lb./hr.} = 230$$

Lb. of liquid per hr. $= 0.050 \times 230 = 11.50$

Work of compression (from Fig. VII.8, three stages assumed)
$$= 2.42 \text{ hp.-hr./lb.-mole of air}$$
$$= 48.5 \text{ hp.-hr./lb.-mole of liquid}$$

The reversible work [by Eq. (X.33)] $= (129.7 + 53) - 540(0.916 - 0)$
$$= -312 \text{ B.t.u./lb.}$$
$$= -3.56 \text{ hp.-hr./lb.-mole}$$

$$\text{Cycle efficiency} = \frac{3.56}{48.5} \times 100 = 7.3 \text{ per cent}$$

(2) H_3 is now 127.5. By Eq. (X.35),

$$\zeta = 0.0321$$
Per cent decrease in liquid yield $= 36$

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[1] From the discussion in Chap. IX it should be evident that only the warm-end temperature difference can be fixed. A cold-end difference is inherent in this process.

[2] The values of the thermodynamic properties of air used in this and subsequent illustrations were obtained from an unpublished diagram. The reader is referred to the following two sources of data: V. Williams, *Trans. Am. Inst. Chem. Engrs.*, **39**, 93–111 (1943). H. Hausen, *Forschungsarbeiten Gebiete Ingenieurwesens*, **274**, 3–48 (1926).

The Williams diagram goes only to 500°R., but a small extrapolation can be made by methods outlined in Chap. VI.

This illustrates the importance of careful insulation and good design of the heat exchanger, since either of the assumed irreversible effects could easily be larger in practice if special care were not taken to reduce them.

(3) $H_1 = 114.5,$ $\zeta = 0.083$
                    Per cent increase in yield = 66

This clearly indicates that pressure is a very important variable.

An increase in pressure is seen to exert a marked influence on the yield of liquid, and the question naturally arises: Will the yield continue to increase with pressure, or will there be a maximum? This question is readily answered as follows:

From Eq. (X.35) one sees that the yield is a maximum when $H_3 - H_1$ is a maximum. H_3 is naturally fixed at the lowest possible pressure and highest possible temperature, and hence H_1 is to be a minimum. The criterion for this is

$$\left(\frac{\partial H_1}{\partial p_1}\right)_{T_1} = T_1\left(\frac{\partial v_1}{\partial T_1}\right)_{p_1} - v_1 = 0$$

or $$T_1\left(\frac{\partial v_1}{\partial T_1}\right)_{p_1} = v_1 \qquad (X.36)$$

This is the fundamental equation of the Joule-Thomson inversion curve (see Chap. VII, page 298), and hence we conclude that the maximum degree of liquefaction occurs when the initial pressure for a given temperature of the gas entering the exchanger is the inversion pressure. This, of course, gives a series of pressures and temperatures (the inversion curve) at which maxima occur; but, assuming the temperature is fixed at 80°F., the best pressure for nitrogen liquefaction would be 375 atm. (see Fig. VII.12).

In the case of hydrogen and helium, it is readily shown by the methods outlined in Chap. VI that the isothermal ΔH of expansion at atmospheric temperature is a negative quantity, and it is impossible to liquefy these gases by this method alone. From the discussion in Chap. VII, it is evident that there is an inversion point of the Joule-Thomson effect which is below room temperature in the case of these two gases. For example, for hydrogen one can readily calculate that at a pressure of 1 atm. the inversion temperature is about 200°K. Consequently, to liquefy this gas by the Joule-Thomson effect, it is necessary to precool the gas at least to this temperature because for any higher temperature the values of μ are negative and it is clear from the relation

$$\Delta H_T = \int_{p_1}^{p_2} \mu C_p \, dp \qquad (X.37)$$

that a negative value of isothermal ΔH must result. For any given

pressure, the limiting value of the temperature above which liquefaction would be impossible can be obtained by calculation (exercise left for the student) from pvT data or an equation of state.[1]

The liquefaction of hydrogen is generally accomplished by precooling the compressed gas by liquid air and then passing it into the usual exchanger and throttle-valve system as shown in Fig. X.17. Helium cannot be liquefied in this manner because its inversion temperature at 1 atm. is probably less than 50°K. and precooling with liquid hydrogen is required.

From an examination of the general form of the inversion curve, it is also evident that for a given pressure of the gas below the maximum inversion pressure the optimum temperature is not the inversion temperature but some lower temperature. This can also be readily seen by reading ΔH values from a TS chart. For example, the following tabulation gives the ΔH change for isothermal expansion of air from 200 to 1 atm. at a series of temperatures:

$T°$K.	$t°$F.	ΔH_T, c.h.u./lb.-mole
300	80	245
270	26	303
240	− 46	420
200	−100	540

From these figures we see that, by precooling air at 200 atm. to −100°F., the yield of liquid air could be more than doubled over the yield obtained merely by water cooling to 80°F. Furthermore, cooling to this temperature can be accomplished by an ordinary vapor-compression cycle using a refrigerant such as ammonia or Freon-12. Since the thermodynamic efficiency of such a process is so much higher than for a cycle utilizing the Joule-Thomson effect, there is also a considerable saving in energy requirement per pound of liquid produced.

A flow sheet of a cycle using these principles is shown in Fig. X.19. Note that, in addition to the refrigerator in which the high-pressure air is cooled by the auxiliary refrigerant, there is also a forecooler utilizing the return low-pressure gas as the cooling agent. Were it not for this added cooler the auxiliary refrigeration system would have to be far larger than otherwise and the returning air would be exhausted at a much lower temperature than necessary, which means a loss in efficiency.

[1] It should be noted, however, that this is a rather severe test of an equation of state. Unless the equation holds accurately over the entire range in question, the result will be very approximate.

The temperature at which the auxiliary refrigerant is evaporated is fixed by the suction pressure of the compressor.   If the refrigerant is Freon-12 and a suction pressure of 1.5 lb. per sq. in. abs. (p_{14}) is maintained, then t_{13} would be about $-100°F$. and t_3 could be $-95°F$., allowing a reasonable Δt for heat transfer.   If atmospheric pressure is the lowest suction pressure desired, then precooling to about $-17°F$. is the
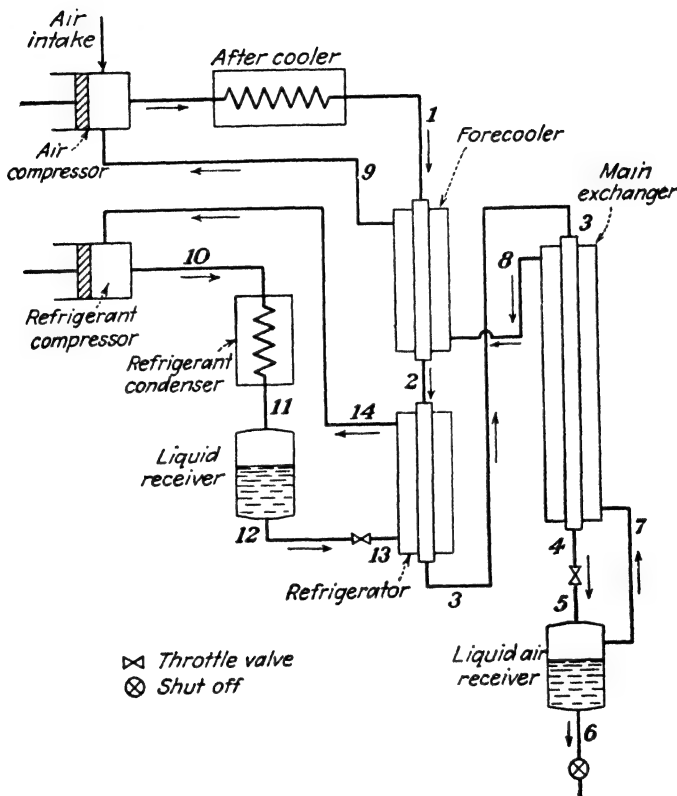
FIG. X.19.—Liquid-air cycle using Joule-Thomson effect supplemented by an auxiliary refrigerator.

best that could be done with this refrigerant.   The fraction of gas liquefied could then be determined by a balance over that part of the system including only the main exchanger, throttle valve, and liquid receiver, which would yield an equation identical with Eq. (X.35). Power requirements for both compressors could then be obtained by methods previously outlined and the thermodynamic efficiency of this cycle determined.

By expanding the compressed gas to be liquefied in two stages as shown in Fig. X.20, the energy requirement can be materially reduced. This can be seen from the fact that the cooling effect ΔH_T in expanding from 200 to 20 atm. at 80°F. is nearly 90 per cent of the cooling obtained in complete expansion to 1 atm., whereas the work to compress from 20 to 200 atm. is much less than from 1 to 200 atm. Consequently, it is
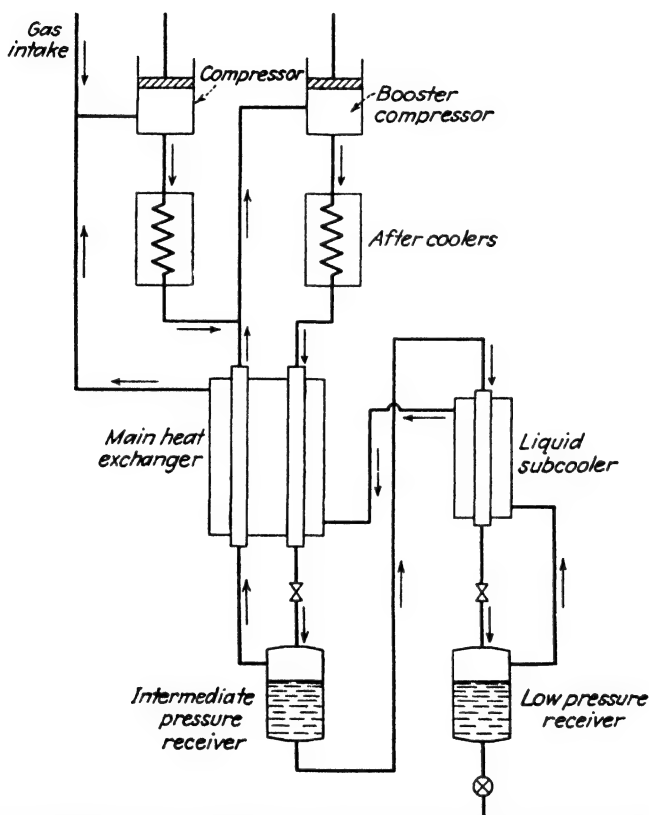
Fig. X.20.—Gas-liquefaction cycle using two-stage Joule-Thomson expansion.

clearly advantageous to expand first to some intermediate pressure and separate the resulting liquid from the gas and then expand this liquid to 1 atm. for removal from the system. In this way the major portion of the gas has to be compressed only from 20 to 200 atm. and a smaller portion over the entire pressure range. A quantitative analysis of such a cycle to determine optimum operating conditions and power requirement can readily be made by methods previously illustrated.

Liquefaction by Engine Expansion (Claude Process).—A liquefaction process using an expansion engine for refrigeration is often called by this name after the French engineer Georges Claude, who pioneered in this field. A simple form of Claude cycle is illustrated in Fig. X.21. As in the case of the Linde cycle it is necessary to use an exchanger with the engine to make the cooling accumulative. It will also be noted that only a portion of the gas is expanded in the engine, the remainder being
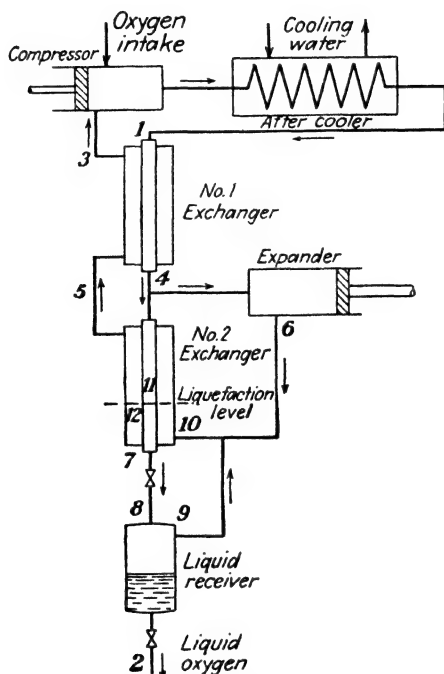
Fig. X.21.—Gas-liquefaction process using an expansion engine.

throttled; hence this process uses a combination of the Joule-Thomson effect and expansion in an engine for refrigeration. If all the gas were expanded in the engine, it would be necessary to produce liquid in the engine, and this is probably undesirable, because it lowers the efficiency. Consequently, a part of the high-pressure gas is passed through an exchanger (often called a "liquefier") countercurrent to gas returning from the liquid receiver and to expanded gas, and liquefied therein.

The analysis of the cycle of Fig. X.21 is considerably more complex than that of the cycle of Fig. X.17 but involves no new principles. One method is developed in the following illustration.

Illustration 12.—Determine a practical set of steady-state conditions for the liquefaction of oxygen by the cycle of Fig. X-21, and estimate the power requirement per pound of liquid produced.

Basis: 1 mole of oxygen entering at (1).

Let ζ = fraction liquefied.

f = fraction of gas that goes to the expander.

e = thermodynamic efficiency of the expander.

ΔH_S = decrease in enthalpy in the engine for an isentropic expansion.

Subscripts will refer to the numbered locations in the figure. For a preliminary analysis, heat leak will be neglected.

Application of the first law to the various units of the system leads to the following equations:

Energy balance on exchanger 1:

$$H_1 - H_4 = (1 - \zeta)(H_3 - H_5) \tag{1}$$

Balances on exchanger 2:

1. Over-all energy balance,

$$(1 - f)(H_4 - H_7) = (1 - \zeta)(H_5 - H_{10}) \tag{2}$$

2. From the liquefaction level to the bottom,

$$(1 - f)(H_{11} - H_7) = (1 - \zeta)(H_{12} - H_{10}) \tag{3}$$

Balance on the liquid receiver:

$$(1 - f)H_7 = \zeta H_2 + (1 - f - \zeta)H_9 \tag{4}$$

By definition of thermodynamic efficiency of the expander,

$$H_4 = H_6 + e \, \Delta H_S \tag{5}$$

Balance at the mixing point ahead of exchanger 2:

$$fH_6 + (1 - f - \zeta)H_9 = (1 - \zeta)H_{10} \tag{6}$$

Assuming that the pressure in the receiver and that of the return gas will always be at 1 atm., the independent variables in these six equations are H_1, H_3, H_4, H_5, H_6, H_7, H_{10}, H_{12}, ζ, f, and e, or a total of 11. Since there are six independent equations we can fix 5 of the above variables and then solve for the rest. There is some latitude in choice of which ones to fix, but assume that we choose to fix the following conditions: p_1, t_1, t_3, e, t_4, and t_{12}, which fixes the 5 variables H_1, H_3, H_4, H_{12}, and e. The basis for fixing t_{12} is the fact that at the level of the dew point of the high-pressure stream there will occur the minimum Δt in this exchanger and, since t_{11} is known once p_1 is fixed, t_{12} can be fixed at some lower value to allow a reasonable Δt, say 5°C.

Solving the six equations simultaneously,

$$\zeta = \frac{(H_3 - H_1)(H_4 - H_{11} - e \, \Delta H_S) + (H_{12} - H_{11})e \, \Delta H_S}{(H_3 - H_2)(H_4 - H_{11} - e \, \Delta H_S) + (H_{12} - H_2)e \, \Delta H_S} \tag{7}$$

$$f = \frac{\zeta(H_3 - H_2) - (H_3 - H_1)}{e \, \Delta H_S} \tag{8}$$

Take the following particular conditions:

$$p_1 = 20 \text{ atm. abs.}$$
$$t_1 = 80°F. \ (300°K.)$$

$$t_3 = 71°F. \ (295°K.)$$
$$e = 0.70$$
$$T_4 = 175°K.^*$$
$$p_6 = 1 \text{ atm.}$$
$$T_{12} = T_{11} - 5 = 133 - 5 = 128°K.$$

From the tables of Millar and Sullivan, one gets the following values (centigrade heat units, pound-moles, and degrees Kelvin): $H_1 = 3,212$; $H_2 = 158$; $H_3 = 3,215$; $H_4 = 2,285$; $H_{11} = 1,859$; $H_{12} = 2,041$; $\Delta H_S = 660$; $H_6 = 1,823$ [by (5). This corresponds to vapor with about 5°C. superheat]; $H_9 = 1,788$.

By (7), $\zeta = 0.122$
By (8), $f = 0.800$
By (1), $H_5 = 2,160$ and $T_5 = 142°K.$
By (3), $H_7 = 800,$ $T_7 = 133$ (mixture of liquid and vapor)

Assuming two-stage adiabatic compression and ideal gas, by Fig. VII.8,

Theoretical work $= 1.570$ hp.-hr./lb.-mole of gas compressed

Assuming 75 per cent over-all compressor efficiency,

Practical work $= 2.09$ hp.-hr./lb.-mole

Shaft work of the expander per lb.-mole O_2 compressed $= fe \ \Delta H_S$
$$= 0.800 \times 0.70 \times 660$$
$$= 369 \text{ c.h.u.}$$
$$= 0.261 \text{ hp.-hr.}$$

Assuming that 90 per cent of this work could be utilized to aid the gas compressor,

Net work required per lb. of liquid oxygen $= \dfrac{2.09 - 0.90 \times 0.261}{0.122 \times 32}$ hp.-hr. $= 0.475$

Thermodynamic efficiency $= \dfrac{0.107}{0.475} \times 100 = 22.6$ per cent

0.107 hp.-hr. is the minimum reversible work for the liquefaction of 1 lb. of oxygen, calculated by the methods previously illustrated.

This determines one set of conditions under which this particular cycle might be expected to operate. The effect of such variables as heat leak, initial pressure, expander-exhaust pressure, expander-intake temperature, and temperature of low-pressure gas leaving the system can readily be investigated by the method illustrated. It is of interest to note that the lower the pressure the lower must be the temperature at intake to the expander for optimum efficiency. Liquid can be made at pressures as low as 5 atm. with reasonable efficiency, though the efficiency is improved at higher pressures. Kapitza[1] has described an air liquefier operating at low pressures that involves several novel features, including

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* This choice is guided by the assumption that the exhaust from the engine should be near saturation and preferably slightly superheated.

[1] KAPITZA, P., *J. Phys.* (*U.S.S.R.*), **1**, 7 (1939).

an expansion turbine and the regenerative type of heat exchanger for both heat transfer and purification.

If one goes in the other direction and raises the pressure, the expander-intake temperature can be increased until with about 200 atm. pressure the expander intake can be at room temperature. This is the basis for the Heylandt process, which is really a combination of the Linde and Claude processes. No details on the Heylandt expander are available, but if the expansion is carried to 1 atm. it seems clear that at least two and preferably three stages of expansion should be used.

The use of engine expansion also makes it possible to liquefy helium without a hydrogen-precooling cycle, as is necessary when the Joule-Thomson effect is used. In fact, it would not be necessary to use any auxiliary refrigeration at all, though in the liquefier developed by Kapitza[1] the compressed helium is precooled by liquid air or nitrogen before entering the helium cycle itself. Without this it would be necessary to use more than one expander. Kapitza developed a reciprocating expander of very clever design that is said to operate under the following conditions:

Intake pressure.	30 atm.
Exhaust pressure....	2.2 atm.
Intake temperature ..	19°K.
Exhaust temperature.........	10°K.

These data correspond to a 60 per cent thermodynamic efficiency based on the Keesom TS diagram for helium.

The Cascade Method.—Although this is one of the earliest methods used for liquefaction of the so-called "permanent gases," it is only recently that it has been applied commercially.[2] At least one large plant in this country is using this process for liquefaction and separation of air, and the most recent application is in the liquefaction of natural gas for storage.[3]

In the case of the two methods of gas liquefaction just discussed, the gas to be processed acts as its own refrigerating medium and usually no external refrigeration is used, though, of course, there are exceptions to this statement. In the case of the cascade process the cooling is generally obtained almost wholly from external circuits and only a small amount from the gas itself. In Fig. X.22 there is shown a three-fluid cascade of ammonia, ethylene, and methane for the liquefaction of air, nitrogen, or oxygen. If the gas were oxygen, it would be necessary to compress it to

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[1] KAPITZA, P., *Proc. Roy. Soc.*, **A147**, 189–211 (1934). See also LANE, C. T., *Rev. Sci. Instruments*, **12**, 326–331 (1941).

[2] For many years the Leyden Cryogenic Laboratory produced liquid air by a cascade process, using as refrigerants methyl chloride, ethylene, and oxygen.

[3] CLARK, J. A., and R. W. MILLER, *Chem. Met. Eng.*, **48**, 74 (1941).

about 100 lb. per sq. in. gauge in order to condense it by methane boiling at 1 atm.; the further cooling to the normal boiling point would come from the evaporation of the liquid oxygen itself. The methane is liquefied by evaporating ethylene, which in turn is liquefied by evaporating ammonia, in its turn liquefied by water cooling.

In the process used at Cleveland, Ohio,[1] for natural-gas liquefaction, there is a two-fluid cascade of ethylene and ammonia, which cools the gas to about $-126°F$. Since the liquid is stored under only a small positive pressure at $-258°F$., it is clear that in this case a considerable
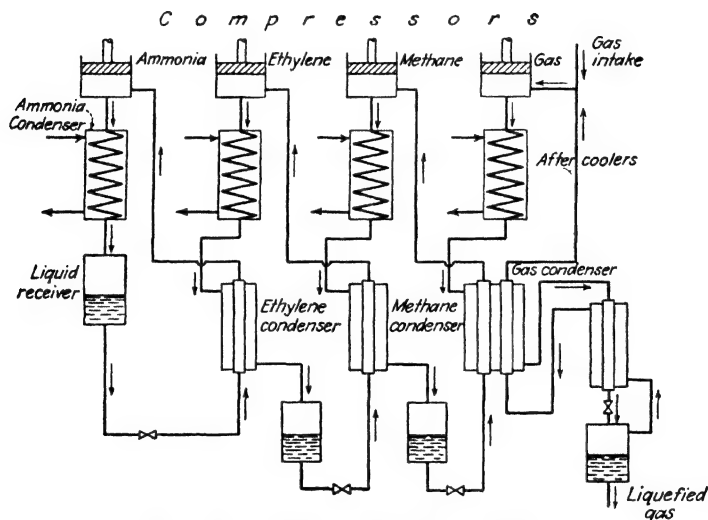
Fig. X.22.—Cascade cycle for gas liquefaction.

proportion of the refrigeration must be performed by the gas itself. It is compressed to 600 lb. per sq. in. to liquefy it by the evaporation of ethylene, and the liquid is then flashed in two stages to reach the final temperature, the flash gas from both steps being used to cool the liquid ahead of the first expansion valve. The two-stage expansion saves power because a portion of the evaporated gas has to be compressed only from this intermediate pressure (55 lb. per sq. in. in this case) to the head pressure of 600 instead of from atmospheric pressure.

Complete analysis of cascade cycles to determine reasonable operating conditions and power requirements can be made by the methods previously presented, with suitable modifications. Limitations of space do not permit the detailed development of a specific case. The chief advantage of the cascade method lies in the fact that it avoids the use

[1] Ref. 3 on page 471.

of any low-temperature engine and since it expands only liquids is less irreversible than a Linde process and hence should operate with a lower power consumption. In very large air-separation plants of the future, the cascade cycle may very likely be the one chosen since power cost will be one of the most important items on the balance sheet.

Gas-separation Processes.—One of the best methods for the separation of a mixture of gases is to utilize the differences in composition of coexisting liquid and vapor phases as applied in the processes of partial condensation and rectification. Such methods must obviously be carried out below the critical temperatures and involve a combination of the methods of liquefaction discussed in the previous sections of this chapter with the methods of bringing about the interaction of the two phases that are commonly comprised in the general term of "distillation." This is the only practicable method in large-scale use at the present time for the separation of air into oxygen, nitrogen, argon, and occasionally some of the rare gases. It has been employed to some extent, especially in other countries, for the separation of various manufactured gases such as water gas and coke-oven gas into hydrogen as the main product with some useful by-products such as ethylene, carbon monoxide, and methane. Competent engineers experienced in this field predict a great expansion of the applications of low-temperature gas separation in the near future.[1] Large-scale use of oxygen or, rather, air enriched in oxygen, in the metallurgical and gas industries may result from improved methods for separating air.

General Principles.—Gas separation requires a method of refrigeration just as gas liquefaction does, since low temperatures must be maintained against heat leak, and the inefficiency of heat exchangers and other equipment operating at levels below room temperature must be compensated for. Consequently, the methods of gas liquefaction discussed above are all applicable to gas separation, with the additional requirement of a rectifying column or other contacting device to bring about a progressive change in composition. Even if there were no heat leak into the apparatus and the heat exchange were perfect, it is evident from Eq. (X.33) that work must be done to separate gases. Though ΔH is substantially zero, ΔS is always greater for a solution than for the pure components.

The minimum work of separation of air into gaseous products at 80°F. and 1 atm., readily calculated by Eq. (X.33), is 0.0239 kw.-hr. per lb. of oxygen or 1.94 kw.-hr. per 1,000 cu. ft. of oxygen (0.161 kw.-hr. per lb.-mole of air). This is considerably less than the work required to liquefy a pound of pure oxygen (0.0800 kw.-hr. per lb.) because there is no refrigeration load in the ideal separation process once it is operating

[1] RUHEMANN, M., *J. Inst. Petroleum*, **28**, 215–239 (1942).

in a steady state. On the other hand, the separation of air into liquid oxygen and gaseous nitrogen requires more energy (0.1036 kw.-hr. per lb. of O_2) than the production of liquid from gaseous oxygen because there is the requirement for heat pumping superimposed on that for gas separation. The best modern plants for air separation require about 12 kw.-hr. per 1,000 cu. ft. of oxygen, and hence their thermodynamic efficiency is about 16 per cent, while a more common figure for a large plant is about 19 kw.-hr., or an efficiency of 10 per cent. It must not be concluded from this, as some have done, that it is relatively easy to bring about a considerable reduction in power requirement by sound application of fundamental principles. There are a considerable number of irreversible effects that cannot be wholly eliminated in any practical process; and the low efficiency of such processes is due, as was clearly shown by Dodge and Housum,[1] to the multiplication of a number of terms of high or moderate efficiency.

Reversible vs. Adiabatic Rectification. One striking illustration of the statement in the preceding paragraph is in the rectification column itself. It will be shown elsewhere (Chap. XIII) that an adiabatic column (this refers to the column proper, excluding boiler and condenser) cannot possibly be reversible no matter how ideally it is operated because reversibility implies phase equilibrium at all levels and this requires a varying liquid and vapor flow in the column instead of the approximately constant molal flow which is characteristic of the adiabatic column. In other words, reversible rectification demands a certain flow distribution, which in turn requires that heat be added at all levels of the ideal column below the feed entrance and removed at all levels above it. For further details on this point reference may be made to the paper by Dodge and
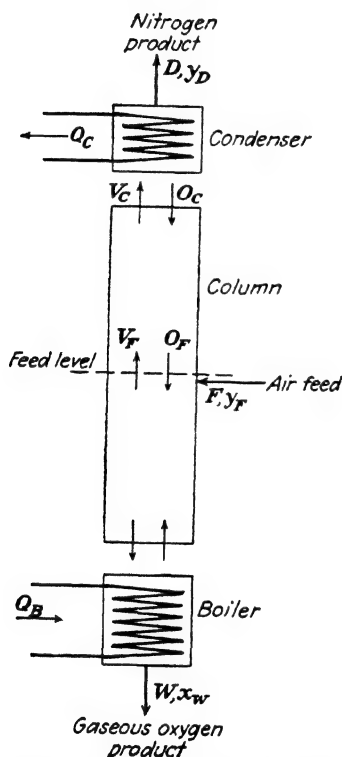
Fig. X.23.—Adiabatic rectification of air.

[1] Dodge, B. F., and C. Housum, *Trans. Am. Inst. Chem. Eng.*, **19**, 117 (1927). This paper may also be consulted for other phases of the subject of air separation.

Housum and to a series of papers by Van Nuys.[1]   The following problem
will aid in illustrating this argument.

Illustration 13.—Calculate the thermodynamic efficiency of an ideally operated
adiabatic rectifying column for separating air into gaseous oxygen and nitrogen.
Estimate the thermodynamic efficiency for practical operation.

In solving this problem it will be necessary to accept at this point some of the
relationships for a rectifying column to be developed in Chap. XIII.   Assume that
saturated vapor of air at 1 atm., containing 21 per cent O_2 and 79 per cent N_2, enters a
column (see Fig. X.23) and is separated into pure nitrogen and oxygen, both saturated
vapors at 1 atm.   Since the column is assumed to be adiabatic, this requires an input
of heat Q_B in a boiler and a removal of heat Q_C in a condenser.   This is true for any
adiabatic column, regardless of temperature level; the mechanism by which these
transfers of heat are accomplished does not concern us in this calculation.

By Eq. (XIII.86) applied to the feed level

$$\frac{O_F}{D} = \frac{y_D - y_F}{y_F - x_F} \tag{1}$$

where O_F/D = ratio of moles of overflow liquid at the level at which the feed enters
to the moles of nitrogen product.   (It will be shown in Chap. XIII that this ratio
is a maximum for the feed level; hence, it is this level which determines the value of
the ratio for the column.)   The minimum possible value of this ratio occurs when the
difference between y_F and x_F is the greatest, or when the two phases are in equilibrium.
Using the equilibrium data of Dodge and Dunbar[2] as summarized by Dodge,[3] one
obtains by substitution in (1)

$$\frac{O_F}{D} = \frac{0 - 0.210}{0.210 - 0.523} = 0.671$$

The value of O_C, the overflow liquid produced in the condenser, is obtained from O_F
by Eq. (XIII.114).   From the available data on enthalpy of oxygen-nitrogen mix-
tures,[4] it can be calculated that

$$\frac{O_C}{O_F} = 1.175$$

Per pound-mole of oxygen product,

$$Q_C = 1.175 \times 0.671 \times 1,335 \times \tfrac{11}{3} \text{ c.h.u.} = 3,960$$

From an over-all energy balance on the whole rectification system (heat leak
assumed zero) we have, per mole of air,

$$Q_B - Q_C = H_F + 0.79H_D + 0.21H_W \tag{2}$$

The available data indicate that the right-hand member of this equation is practically
zero, and therefore

$$Q_B = Q_C \tag{3}$$

[1] Van Nuys, C. C., *Chem. Met. Eng.*, **28**, 207–210, 255–256, 311–313, 359–362
(1923).

[2] Dodge, B. F., and A. K. Dunbar, *J. Am. Chem. Soc.*, **49**, 501 (1927).

[3] Dodge, B. F., *Chem. Met. Eng.*, **35**, 622 (1928).

[4] See Fig. IX.14.

The net requirement, thermodynamically speaking, for the operation of the adiabatic column is that 3,960 c.h.u. must be removed from the condenser and the same quantity added to the boiler, based on 1 lb.-mole of gaseous oxygen product. Since this is a heat pumping operation, work is required to accomplish it and the minimum is given by the relation

$$W = QT_0 \left(\frac{1}{T_{N_2}} - \frac{1}{T_{O_2}} \right) \tag{4}$$

which is readily derived from previous considerations of the Carnot cycle. T_0 is the lowest temperature at which heat can be rejected (assume it is 300°K.); T_{N_2} and T_{O_2} are the normal boiling points of nitrogen and oxygen, respectively. Substituting values,

$$W = 3,960 \times 300 \left(\frac{1}{77.3} - \frac{1}{90.2} \right)$$

$$= 2,160 \text{ c.h.u.}$$

$$= 2.89 \text{ kw.-hr./1,000 cu. ft. of } O_2 \text{ at 80°F. and 1 atm.}$$

It has been shown by Van Nuys[1] that the heat exchange between the incoming air and the outgoing products can be accomplished reversibly without expenditure of any work; therefore, the above figure represents the least amount of work for air separation with an adiabatic column but with all other parts of the system reversible. In other words, no process using an adiabatic column can have a thermodynamic efficiency greater than

$$\frac{1.94}{2.89} \times 100 = 67 \text{ per cent}$$

Now, if we allow 20 per cent greater than the minimum reflux (minimum reflux requires an infinite column) and allow an average temperature difference of 3°C. in the boiler and the condenser for reasonable rate of heat transfer, the thermodynamic efficiency is

$$\frac{1,452}{3,960 \times 1.2 \times 300[(1/74.3) - (1/93.2)]} \times 100 = 37.5 \text{ per cent}$$

(1,452 is the minimum work of separation in centigrade heat units per pound-mole of oxygen.)

One can conclude that any air-separation system including an adiabatic column with reasonable operating conditions *starts* with an efficiency of less than 40 per cent even if the whole refrigeration system is reversible. Hence, it is not surprising that the best processes have efficiencies of less than 20 per cent.

General Balance Equations.—The over-all result of any air-separation process is represented diagrammatically in Fig. X.24. All three of the methods of producing refrigeration at low temperatures are considered in this general case. The usual three balances can be written as follows:

$$N_1 = N_2 + N_3 \tag{X.38}$$

$$N_1 y_1 = N_2 y_2 + N_3 y_3 \tag{X.39}*$$

$$N_1 H_1 = N_2 H_2 + N_3 H_3 + W_E + Q_R - Q_L \tag{X.40}$$

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[1] VAN NUYS, C. C., *Chem. Met. Eng.*, **28**, 408–413 (1923).

* For a liquid-oxygen process, y_2 should be changed to x_2.

If we assume that the mixtures represented by the two products are ideal solutions when both products are gaseous, then

$$H_2 = H_{O2}y_2 + H_{N2}(1 - y_2) \tag{X.41}$$

and
$$H_3 = H_{O3}y_3 + H_{N3}(1 - y_3) \tag{X.42}$$

where H_{O2}, H_{N2}, and the similar terms with subscript 3 are enthalpies of pure oxygen and nitrogen, respectively.
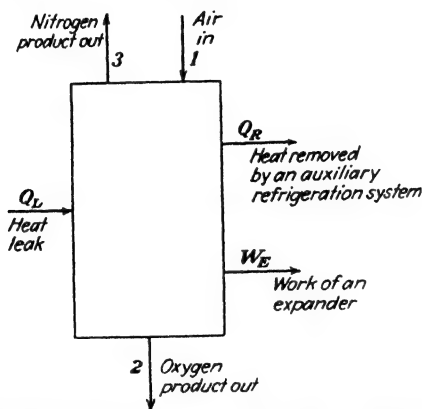
Fɪɢ. X.24.—Over-all energy and material balances on an air separation process.

Now let $p_2 = p_3$ and $T_2 = T_3$. Then

$$H_{O2} = H_{O3} = H_O$$
$$H_{N2} = H_{N3} = H_N$$

Algebraic combination of these various equations gives

$$H_1 = y_1(H_O - H_N) + H_N + q_A \tag{X.43}$$

where
$$q_A = \frac{W_E + Q_R - Q_L}{N_1} \tag{X.44}$$

From Eq. (X.43) one notes that, if W_E and Q_R are zero, H_1 is determined only by the heat leak and the state of the gases leaving the low-temperature system; when these two things are fixed, the operating pressure is fixed. When one of the products is liquid oxygen, the situation is quite different, for the pressure is no longer fixed when these two variables are; on the contrary, it is a function of the composition of the nitrogen leaving, which in turn is related to the yield of liquid. This is shown as follows:

Simultaneous solution of the three balance equations coupled with Eq. (X.42) gives

$$y_3 = \frac{y_1(H_{N3} - H_2) - x_2(H_{N3} - H_1 + q_A)}{(x_2 - y_1)(H_{O3} - H_{N3}) + H_1 - H_2 - q_A} \tag{X.45}$$

and we see that H_1 (and hence p_1) is a function of y_3 when q_4 and the state at 3 are fixed.   The yield of liquid or of gaseous oxygen defined as the ratio of the oxygen in the product to the total oxygen in the air is given by

$$\text{Per cent yield} = \frac{100x_2N_2}{0.21N_1} = \frac{100x_2}{0.210}\left(\frac{0.210 - y_3}{x_2 - y_3}\right) \qquad \text{(X.46)}$$

Simple Linde Process.—Such a process for separation of air into gaseous oxygen and nitrogen is shown in Fig. X.25.   The air is com-
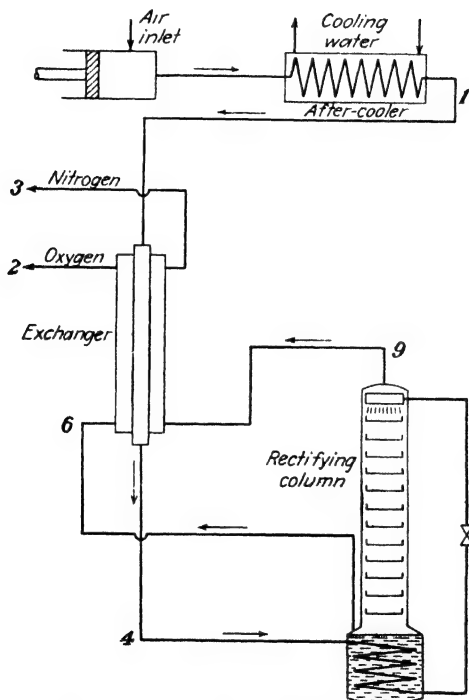
Fig. X.25.—Simple Linde cycle for air separation.

pressed and water-cooled and then further cooled by heat exchange with the separated gases leaving the column.   The cold compressed air (plus a small amount of liquid to compensate for heat leak into the column) enters a heat exchanger in the boiler, where it liquefies, thus giving up heat to the boiling liquid oxygen.   The liquid air is then expanded into the top of the column, and the liquid is rectified in the usual manner.   It will be noted that the nitrogen leaving the top of the tower will be quite impure since the lowest oxygen content it could

possibly have is that for phase equilibrium with liquid air, which is 6.4 per cent O_2. Actually, owing to flashing at the expansion valve and to other causes, the nitrogen will be not better than about 92 per cent pure, and the maximum recovery of oxygen is about 65 per cent. A cycle for producing liquid oxygen would be similar, the only difference on the diagram being that liquid oxygen is withdrawn from the boiler and there is no return stream of oxygen in the exchanger. The following illustration will bring out some of the differences between a gaseous and a liquid process and will also show the application of some of the equations developed above.

Illustration 14.—Determine reasonable operating conditions for a simple Linde air-separation process producing gaseous products. Repeat for a process yielding liquid oxygen. Also, report the power requirement in kilowatt-hours per pound of oxygen and the thermodynamic efficiency. Assume a heat leak into the low-temperature system of 50 c.h.u. per lb.-mole of air. The oxygen product is to be 99.5 per cent pure.

Basic Assumptions.

1. Air enters the low-temperature system at 80°F.
2. Minimum allowable Δt in exchangers is 5°C.
3. Maximum practicable recovery of oxygen as oxygen product in a column of the type shown in Fig. X.25 is 65 per cent.
4. Both products leave the system at 1 atm. abs.
5. Pressure drop due to fluid flow is neglected.
6. Over-all power efficiency of compressor based on isentropic compression is 75 per cent.
7. Mass basis is 1 lb.-mole of air.

Gaseous Oxygen.—$H_O = 3,215$; $H_N = 2,850$; and $q_A = -50$ (note that W_E and Q_R are 0 for this cycle).

By Eq. (X.43), $H_1 = 0.210(3,215 - 2,850) + 2,850 - 50$
$= 2,877$

From a TS diagram for air, $p_1 = 59$ atm.

It should be noted that this figure depends very largely on the amount of heat leak and would be quite different for other assumed values of the leak.

Assuming three-stage compression, the theoretical work of compression from Fig. VII.8 = 2.10 hp.-hr. per lb.-mole or the practical work = 2.09 kw.-hr. per lb.-mole.

By Eq. (X.46), $y_3 = 0.0852.$

The minimum work of separation into products of the above compositions is 0.0820 kw.-hr. per lb.-mole of air, and hence the thermodynamic efficiency is only 3.9 per cent.

To determine the conditions under which the heat exchanger operates, a balance around it is made as follows:

$$N_1(H_1 - H_4) + Q_{L_1} = N_2(H_2 - H_6) + N_3(H_3 - H_9) \tag{1}$$

Assume 30 per cent of the total heat leak is into the exchanger and 70 per cent into the column, or $Q_{L_1}/N_1 = 15$ c.h.u.

$$\frac{N_2}{N_1} = 0.137 \quad \text{and} \quad \frac{N_3}{N_1} = 0.863$$

$H_2 = 3,215; \ H_3 = 0.0852(3,215) + 0.9148(2,849) = 2,884; \ H_6 = 1,788; \ H_9 = 1,379.$

Substituting these values in (1),

$$H_4 = 1,397$$

and from the chart the temperature T_4 is 149°K. T_4 is considerably greater than either T_6 or T_9, and therefore we can be reasonably certain that there is no violation of the second law anywhere in the exchanger.

As a partial check on the calculations it is well to make a heat balance on the column, thus:

$$1,397 + 35 = 0.863(1,379) + 0.137(1,788)$$
$$1,432 = 1,434 \qquad \text{(check)}$$

Liquid Oxygen.—For this case there is no one operating pressure but a series of pressures related to liquid yields. For the purpose of the illustration, only one condition will be chosen, *viz.*, $p_1 = 200$ atm.

Substituting values in Eq. (X.45),

$$y_2 = \frac{0.210(2,849 - 158) - 0.995(2,849 - 2,721 - 50)}{(0.995 - 0.210)(3,215 - 2,849) + 2,721 - 158 + 50} = 0.168$$

By Eq. (X.46),   Per cent liquid yield $= 24$

Assuming four-stage compression, the theoretical work of compression $= 3.83$ hp.-hr. per lb.-mole of air or the practical work $= 3.81$ kw.-hr.

The minimum work of separation by Eq. (X.33) $= 613$ c.h.u. per lb.-mole of air $= 0.324$ kw.-hr. The thermodynamic efficiency $= 8.5$ per cent.

From a balance of the exchanger, we find $H_4 = 1,326$ from which $T_4 = 170$°K.

The liquid-oxygen cycle would not operate at all under the pressure found sufficient to operate the gaseous-oxygen cycle. Even at the high pressure of 200 atm. the yield is very low, and the air requirement per unit of liquid produced would be excessive. There are several ways in which the yield of the liquid cycle can be improved and/or the pressure reduced that are suggested by the previous discussion on liquefaction. Two common methods are (1) use of auxiliary refrigeration and (2) use of an expansion engine. Analyses of such cycles are beyond the scope of this book, but anyone can readily carry them out by the methods outlined above.

Rectification at Low Temperatures.—Although the process of rectification is, in general, the same at low temperatures as at temperatures above the level of the room, it differs in a few important particulars that are interesting from a thermodynamic standpoint. In the first place, the heat input to the boiler and the heat output in the condenser are quite independent in ordinary rectification, but at low temperature they must be very definitely tied together in the usual cycle in which the refrigerating medium is the gas which is being separated. The heat input to the boiler in the latter case cannot come from any source indiscriminately if efficient operation is desired but must be heat that has to be removed

elsewhere from the system. It amounts to this: the heat removed in the condenser to produce reflux is the only heat that can be added to the boiler. Generally, the reflux condenser and the boiler are combined into one; they will then be referred to as the "condenser-boiler." In the second place, the production of a reflux liquid nitrogen, which is essential for complete separation, involves certain difficulties and has given rise to certain special designs of columns that it seems worth while to discuss from the standpoint of principles.
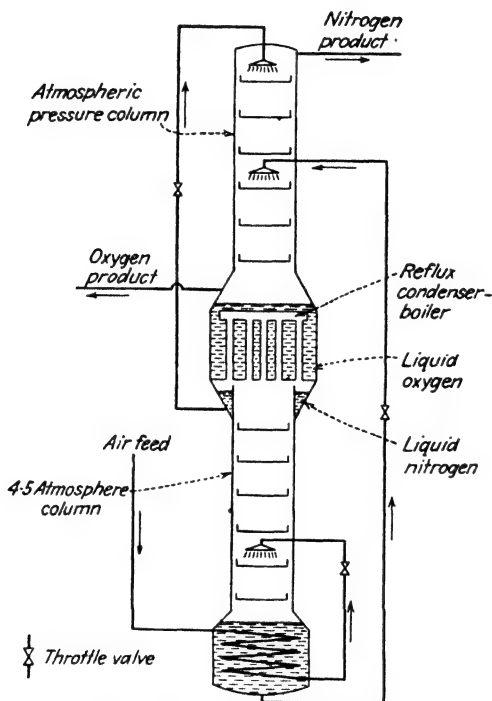
Fig. X.26.—Linde double column.

The so-called "single column" is one in which the air under elevated pressure enters a heat exchanger immersed in a pool of liquid oxygen below the column and liquefies there, giving up its heat to boil the oxygen. The liquid so produced is then fed to the top plate of the column. This is simply the exhausting column of ordinary distillation practice; it obviously cannot produce pure nitrogen or recover a high percentage of the oxygen in the air.

There are about five different ways in which a substantially pure liquid-nitrogen reflux can be produced for an enriching section of the

column. These are (1) evaporation of liquid oxygen at a reduced pressure; (2) use of an external nitrogen-liquefaction cycle; (3) use of an auxiliary refrigerant such as helium or neon; (4) partial condensation of the air feed in a condenser-boiler, with a means of separating into two fractions one of which is rich in nitrogen; and (5) use of a double column. Methods 1, 2, and 3 are believed to have been used but are probably of minor importance at the present time and will not be discussed in further detail. Method 4 is the essence of the original *retour en arrière* condenser of Claude, which is still in use. Method 5 is the most important from a practical standpoint and will be discussed briefly with the aid of Fig. X.26, which illustrates the principle of the double column first developed by Linde.

The double column consists of a column operating at elevated pressure surmounted by an atmospheric-pressure column. The boiler of the upper column is at the same time the reflux condenser for both columns. Gaseous air plus enough liquid to take care of heat leak into the column (more liquid, of course, if liquid-oxygen product is withdrawn) enters the exchanger at the base of the lower column and condenses, giving up heat to the boiling liquid and thus supplying the vapor flow for this column. The liquid air enters an intermediate point in this column as shown. The vapors rising in this column are partially condensed to form the reflux, and the uncondensed vapor passes to an outer row of tubes and is totally condensed. the liquid nitrogen collecting in an annulus as shown. By operating this column at 4 to 5 atm. the liquid oxygen boiling at 1 atm. is cold enough to condense pure nitrogen. The liquid that collects in the bottom of the lower column contains about 45 per cent O_2 and forms the feed for the upper column. Such a double column can produce a very pure oxygen with high oxygen recovery or a very pure nitrogen with oxygen of moderate purity. It cannot produce both products simultaneously in a high state of purity owing primarily to the fact that air is really a ternary mixture and the argon must be taken off with one of the products.[1]

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[1] For further details on air separation, gas liquefaction, and related subjects the following references are suggested: RUHEMANN, M., "The Separation of Gases," Oxford, Clarendon Press, New York, 1940. "Handbuch der Experimental Physik," WIEN, W., and F. HARMS, Vol. IX, Leipzig, 1929, section entitled "Gasverflüssigung und ihre thermodynamischen Grundlagen, pp. 47–185. H. Lenz. RUHEMANN, M., and B. RUHEMANN, "Low Temperature Physics," Cambridge University Press, London, 1937.

CHAPTER XI

CHEMICAL REACTION EQUILIBRIUM

The chemical engineer who is concerned with the design or operation of equipment in which chemical reactions take place or who is developing new processes involving chemical change not only should have a thorough understanding of the fundamental factors which control reactions but should also know how to utilize such information to aid in the solution of problems arising in practice. It is the purpose of this chapter to review the most important relationships that govern equilibria in chemical reactions and to apply the principles and the equations expressing them to typical reactions that are either of actual or potential importance to industry.

EQUILIBRIUM AND REACTION RATES

Practically all questions about any given chemical reaction can be grouped under two fundamental factors, (1) equilibrium yield and (2) rate of reaction. It is very important at the outset to get these two factors clearly differentiated. Given a reaction such as

$$CO + H_2O = CO_2 + H_2 \qquad (XI.1)$$
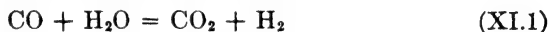
one wants to know to what extent the reaction will proceed in a certain time under a given set of conditions. The most important conditions that can be controlled by the operator are (1) temperature, (2) pressure, (3) ratio of reactants, and (4) catalyst. The effects of these various controllable factors can be understood only by separating them into the two distinct categories of (1) effect on reaction rate and (2) effect on equilibrium. Unless this separation is made, the observable facts pertaining to any reaction appear confusing and seem to have no meaning.

The rate at which a reaction will proceed is obviously of the utmost importance from an industrial standpoint. A reaction proceeding very slowly would require such large and expensive equipment to permit the realization of a reasonable production that it would be entirely uneconomical. But it is equally important to know what the maximum possible extent of the reaction can be under a given set of conditions. Much time has been uselessly expended in attempts to speed up reactions that could not possibly occur to the extent desired at any speed.

It will be assumed that every reaction is a reversible one, *i.e.*, can proceed to some extent in either direction, depending on the conditions.

Perhaps a more exact statement of this would be that every reaction has a certain *tendency* to proceed in one direction or the other. In other words, using reaction (XI.1) as an example, if pure CO and pure H_2O are brought together, there will be some CO_2 and H_2 formed under any conditions. The amounts formed in any reasonable time might be too small to detect by the most delicate analytical methods, but we can nevertheless regard them as actually being present. Similarly, if we bring pure CO_2 and H_2 together, we shall assume that some CO and H_2O are formed.

In any case of chemical reaction it is often exceedingly difficult to distinguish by experiment between a system in true equilibrium and therefore with no tendency to change and a system that is simply inert, *i.e.*, in which there is present something analogous to mechanical friction and the rate of change is too small to detect. In either case the rate of any change might be so small that one could not detect it in any reasonable time. If we attempt to speed up the rates by increasing the temperature, then we cannot tell how much of the effect observed is due to a change in rate and how much to a shift in the equilibrium state. Thermodynamics furnishes us with a means of predicting driving forces and hence equilibrium states so that we do not need to depend on experiment to make this distinction. The development and utilization of these methods form the chief subject matter of this chapter.

It is of considerable practical importance to be able to make this distinction, for if a reaction does not proceed to a practicable extent in a given time under a certain set of experimental conditions, there is always the possibility of finding some way to make it go if rate is the limiting factor; but if it does not proceed because it is close to equilibrium, then it will be necessary to modify the conditions so as to shift the equilibrium point in the direction desired.

As we have mentioned early in this book from a general viewpoint and should emphasize again here for the special case of chemical reaction, the rate at which a chemical reaction proceeds bears no definite relation to the driving force or tendency for change. An understanding of the factors affecting both is essential to an interpretation of what actually is observed when conditions for a reaction exist. Whereas thermodynamics provides useful tools for determining the driving forces and the effect of various factors on them, *it cannot give any information on reaction rates.* This fact must be clearly grasped. Lack of an appreciation of it has resulted in much confusion and in false conclusions about reactions. That thermodynamics, in the usual sense of the word, could predict nothing about rates is evident from the fact that it deals essentially with differences between state functions and is not concerned with the mechanism or the path by which a change between two states occurs.

Of the four important factors mentioned as controlling the course of a reaction, three of them will affect both the rate and the driving force

but the fourth, a catalyst, will affect only the rate. This statement needs some qualification; it is strictly true only for the case of heterogeneous or contact catalysis, *i.e.*, where the catalyst or contact agent is in a different phase from the reacting substances. In the case of homogeneous catalysis, the catalyst does affect the driving force or the states of equilibrium because it will have an effect on the activities of the reactants.

The relationship between rates and driving forces may be further elucidated by considering the interpretation of a common observation concerning the course of a reaction that is illustrated in Fig. XI.1. These particular observations are for the reaction $CO + 2H_2 = CH_3OH$, but similar ones apply to practically all reactions. In almost all cases (exceptions are rare and not yet well understood), reaction rate increases with increase in temperature. Driving force, on the other hand, may either increase or decrease. Practically all reactions involving synthesis (formation of compounds from elements or simpler compounds) show a decrease in driving force with increase in temperature, and vice versa for decomposition reactions. Below a certain temperature level the rate of reaction may be so small that no appreciable conversion of reactants to products occurs in a given time in spite of a considerable driving force. As the temperature is increased, other things being equal,

Fig. XI.1.—Influence of equilibrium and reaction rate on the course of a reaction.

the rate increases very rapidly and conversion increases, as shown in the figure, although the driving force is getting less. Finally, a temperature level is reached at which the effect of driving force in reducing the conversion predominates over the opposite effect of rate and the conversion passes through a maximum. Presumably all reactions show this general course, but the shape of the curve and the temperature of the maximum point would vary enormously.

As a further illustration of the importance of a clear understanding of the influence of these two factors, let us consider briefly the interpretation of certain experimental observations on the ammonia synthesis reaction. The facts to be interpreted are as follows:

1. When N_2 and H_2 are brought together at atmospheric pressure and room temperature, no detectable amount of NH_3 is formed either in the presence or absence of catalysts.

2. When N_2 and H_2 are brought together at 450°C. and 1 atm. in the presence of catalysts, a small trace of NH_3 is formed.

3. When N_2 and H_2 are brought together at 450°C. and 100 atm. pressure in the absence of a catalyst, no NH_3 is formed.

4. When the conditions of (3) obtain and a catalyst is present, about 16 per cent of NH_3 would be formed, starting from gases in the stoichiometric ratio and allowing sufficient time of contact.

The interpretation of these facts from the standpoint of equilibrium and reaction rate is as follows:

1. Rate is the controlling factor. Almost complete conversion to NH_3 would occur if the reactants could be activated in some way.

2. Equilibrium is the controlling factor. The rate is high, but the maximum possible conversion corresponds to about 0.2 per cent NH_3 in the gas.

3. Rate is the controlling factor, since appreciable reaction could occur, as shown by (4).

4. Both rate and equilibrium are important. Equilibrium limits the NH_3 to 16 per cent, but short times of contact with the catalyst would result in a much smaller percentage.

Without a knowledge of the equilibrium in this and similar reactions, observations such as these would be mystifying, and one could easily waste considerable time and energy in attempting to achieve the impossible.

Knowing the equilibrium states for any chemical system as a function of the three independent variables—pressure, temperature, and initial reactant ratio—one can predict the equilibrium or maximum possible degree of conversion. The maximum degree of conversion will be attained only when the system has reached equilibrium, which will require an infinite time. The maximum conversion is therefore the asymptotic limit that the degree of conversion can approach but never quite reach. Nevertheless, it is of great practical importance since it establishes an absolute limit beyond which one cannot go and it furnishes a yardstick for the comparison of different procedures for carrying out a given reaction.

The closeness of the approach to equilibrium conversion in any actual case will depend on many factors and will vary with every individual case. Economic as well as purely technical factors come into play when reactions in industry are considered. Degree of conversion must frequently be sacrificed to obtain a greater total production in a given time. In spite of this, a knowledge of the best possible conversion from any reaction under various conditions is of the greatest importance.

In all the treatment of this chapter, we shall deal only with spontaneously occurring reactions. Reactions induced by special forces such as e.m.fs. will be considered as outside the scope of this text.

FUNDAMENTAL RELATIONSHIPS

Some of the equations for chemical equilibrium derived in Chap. IV are assembled here for convenient reference. They are written on the basis of the generalized reaction

$$aA + bB + \cdots = lL + mM + \cdots \qquad (XI.2)$$

The general mass-action equations applying to both homogeneous and heterogeneous equilibria are

$$\frac{(\bar{a}_L)^l(\bar{a}_M)^m \cdots}{(\bar{a}_A)^a(\bar{a}_B)^b \cdots} = K_a \quad \text{[from Eqs. (IV.241) and (IV.243)]} \quad (XI.3)$$

$$\Delta\mu^\circ = -RT \ln K_a \qquad (IV.244)$$

or if the standard state for each substance involved in the reaction is that of the pure component at the given p and T, we can write

$$\Delta F^\circ = -RT \ln K_a \qquad (IV.245)$$

For the special case of homogeneous gaseous reactions when the standard state of each gas is one of unit fugacity, we have

$$\frac{(\bar{f}_L)^l(\bar{f}_M)^m \cdots}{(\bar{f}_A)^a(\bar{f}_B)^b \cdots} = K_f \qquad (IV.247)$$

This equation is really identical with Eq. (XI.3) because $a = f$ for a gas as a result of the way in which the standard state is commonly defined. The equation analogous to Eq. (IV.245) is

$$\Delta F^\circ = -RT \ln K_f \qquad (XI.4)$$

For the special case of reaction in ideal gaseous solution (not ideal gases),

$$\frac{(x_L f_L)^l(x_M f_M)^m \cdots}{(x_A f_A)^a(x_B f_B)^b \cdots} = K_f \qquad (IV.251)$$

For reaction in ideal liquid solution,

$$\frac{(x_L)^l(x_M)^m \cdots}{(x_A)^a(x_B)^b \cdots} = K_x \qquad (IV.250)$$

For reaction between ideal gases,

$$\frac{(x_L)^l(x_M)^m \cdots}{(x_A)^a(x_B)^b \cdots} = p^{-\Sigma n}K_{p^\circ} \quad \text{[from Eq. (IV.249)]} \quad (XI.5)$$

Equations (IV.251) and (IV.253) were combined and put in the form

$$\frac{K_f}{K_p} = K_\gamma = \frac{(\gamma_L)^l(\gamma_M)^m \cdots}{(\gamma_A)^a(\gamma_B)^b \cdots} \qquad (IV.254)$$

where $\gamma = f/p$ (or a/p).

Note that K_γ is independent of the composition of the equilibrium mixture but is a function of p and T. K_γ is useful in giving a quick picture of the extent of the deviation from the simple ideal-gas case for which K_γ would have the value 1.0 at all temperatures and pressures.

At low pressures where all actual gases may be assumed ideal, Eqs. (XI.3), (IV.247), (IV.251), and (XI.5) are identical when applied to a homogeneous gas reaction, and hence

$$K_p = K_{p^\circ} = K_f = K_a$$

p° referring to a limiting pressure at which all gases may be assumed ideal.

For a dilute solution, activity may be assumed proportional to concentration (see Chap. IV), and the general equation (XI.3) reduces to Eq. (IV.251) for this case, also.

Another equilibrium constant is defined by the equation

$$K_c = \frac{(C_L)^l(C_M)^m \cdots}{(C_A)^a(C_B)^b \cdots} \tag{XI.6}$$

For ideal gases,

$$C_i = \frac{N_i}{V} = \frac{\bar{p}_i}{RT} = \frac{p x_i}{RT} \tag{XI.7}$$

From Eqs. (XI.5) to (XI.7) we have, for the case of ideal gases,

$$K_p = K_c(RT)^{\Sigma n} \tag{XI.8}$$

Since, for any solution,

$$C_i = x_i \frac{N}{V} \tag{XI.9}$$

Equation (IV.250), applying to an ideal-liquid solution, may be written

$$\frac{(C_L)^l(C_M)^m \cdots}{(C_A)^a(C_B)^b \cdots} \left(\frac{V}{N}\right)^{\Sigma n} = K_x \tag{XI.10}$$

If the solution is dilute with respect to all the reaction components, V/N will not change much as the individual concentrations change, and it may be combined with the constant, giving the same equation as Eq. (XI.6).

Dependence of the equilibrium constant on the temperature is given, in general, by

$$\frac{d \ln K_a}{dT} = \frac{\Delta \bar{H}^\circ}{RT^2} \tag{IV.258}$$

where $\quad \Delta \bar{H}_0 = l\bar{H}_L^\circ + m\bar{H}_M^\circ + \cdots - a\bar{H}_A^\circ - b\bar{H}_B^\circ - \cdots \tag{IV.259}$

When the standard state of each substance is the pure state at the given p and T, Eq. (IV.258) becomes

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{IV.260}$$

EFFECT OF TEMPERATURE

From the broad principles of equilibrium it can be deduced that, if a change occurs in one of the variables determining the state of equilibrium, the equilibrium will shift in such a way as to tend to annul the change. Applied to chemical equilibrium, this is sometimes known as the Le Châtelier–Braun principle. In the case of temperature as the variable, it means that an increase in temperature will shift the equilibrium state in the direction of an absorption of heat. Thus an endothermic reaction will be favored (*i.e.*, equilibrium shifted so as to cause the reaction to proceed further) by an increase in temperature, and vice versa.

The quantitative effect is given by Eqs. (IV.258) and (IV.260); since these are both the same in general form, we shall choose the latter for further development.

From Chap. IX we have[1]

$$\Delta H = \Delta H_0 + \Delta\alpha T + \tfrac{1}{2}\Delta\beta T^2 + \tfrac{1}{3}\Delta\gamma T^3 + \cdots \quad \text{(IX.101)}$$
$$\Delta\alpha = l\alpha_L + m\alpha_M + \cdots - a\alpha_A - b\alpha_B - \cdots \quad \text{(XI.11)}$$

and similarly for the other coefficients of Eq. (IX.101).

ΔH_0 is merely a constant of integration whose value is obtained from one known value of ΔH.

Substituting Eq. (IX.101) in Eq. (IV.260),

$$\int d \ln K_a = \int \left[\frac{\Delta H_0}{RT^2} + \frac{\Delta\alpha}{RT} + \frac{1}{2}\frac{\Delta\beta}{R} + \frac{1}{3}\frac{\Delta\gamma}{R} T \right] dT \quad \text{(XI.12)}$$

Integrating,

$$\ln K_a = -\frac{\Delta H_0}{RT} + \frac{\Delta\alpha}{R}\ln T + \frac{1}{2}\frac{\Delta\beta}{R} T + \frac{1}{6}\frac{\Delta\gamma}{R} T^2 + C \quad \text{(XI.13)}$$

From Eqs. (IV.245) and (XI.13)

$$\Delta F^\circ = \Delta H_0 - \Delta\alpha T \ln T - \tfrac{1}{2}\Delta\beta T^2 - \tfrac{1}{6}\Delta\gamma T^3 + IT \quad \text{(XI.14)}$$

where $I = -RC$. C and I are integration constants whose values are determined from one known value of K_a or ΔF°.

It is evident from these equations that, if the specific heats of all the reacting substances are accurately known as a function of temperature and if the heat of reaction is known at some one temperature, there is no point in determining an equilibrium constant at more than one temperature because one value suffices to determine C (or I) and hence the whole course of K_a as a function of T.

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[1] The superscript [°] indicating the standard state will be dropped from ΔH in all subsequent equations in the interests of simplicity.

If the heat of reaction is not available or is of doubtful accuracy and if values of K_a have been determined over a range of temperatures, the following procedure is useful:

Rearrange Eq. (XI.13) to

$$\frac{\Delta H_0}{T} + I = -R \ln K_a + \Delta \alpha \ln T + \frac{1}{2} \Delta \beta T + \frac{1}{6} \Delta \gamma T^2$$

Plot the right-hand side of this equation vs. $1/T$, and draw the best straight line through the points. The slope of this line gives ΔH_0 and the intercept gives I. In this way an equation for the equilibrium constant as a function of T is obtained, and at the same time one obtains the heat of reaction.

Illustration 1.—Newton and Dodge[1] measured the equilibrium constant K_p for the reaction $CO + 2H_2 = CH_3OH$ at a pressure sufficiently low so that all the reacting substances may, with little error, be regarded as ideal gases. The average value of a number of determinations gave $K_p = 2.32 \times 10^{-3}$ at 250°C. What are the standard free-energy change and the equilibrium constant for this reaction at 500°C.?

To evaluate ΔH_0 and the specific-heat coefficients, the following data are available: Heats of combustion at 25°C.:

$$\begin{align} H_2, \Delta H &= -68,313 \text{ g.-cal./g.-mole} \\ CO, \Delta H &= -67,623 \text{ g.-cal./g.-mole} \\ CH_3OH(g), \Delta H &= -182,560 \text{ g.-cal./g.-mole} \end{align}$$
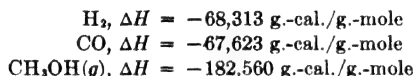
(H_2O is taken as liquid in all cases.)

From these data, ΔH for the methanol synthesis reaction at 25°C. $= -21,690$.

Molal heat capacities at constant pressure:

$$\begin{align} H_2, C_p &= 6.65 + 0.00070T \\ CO, C_p &= 6.89 + 0.00038T \\ CH_3OH, C_p &= 2.0 + 0.03T \end{align}$$

C_p is in gram-calories per degree Centigrade and T in degrees Kelvin.

$$\begin{align} \Delta \alpha &= 2.0 - 2(6.65) - 6.89 = -18.19 \\ \Delta \beta &= 0.03 - 2(0.00070) - 0.00038 = 0.0282 \\ \Delta \gamma &= 0 \end{align}$$

Utilizing these data and Eq. (IX.101),

$$\Delta H_0 = -17,530$$

Since we are assuming ideal gases, $K_p = K_a$. Substituting $K_a = 2.32 \times 10^{-3}$ at $T = 523$ in Eq. (XI.13),

$$\begin{align} C &= 30.67 \\ I &= -1.987 \times 30.67 = -60.94 \end{align}$$

From Eqs. (XI.13) and (XI.14), at 500°C.,

$$\begin{align} K_a &= 1.60 \times 10^{-4} \\ \Delta F° &= 20,510 \end{align}$$

[1] Newton, R. H., and B. F. Dodge, *J. Am. Chem. Soc.*, **56**, 1287–1291 (1934).

If ΔH may be assumed to be a constant, independent of the temperature, integration of Eq. (IV.260) gives

$$\ln K_a = -\frac{\Delta H}{RT} + C \tag{XI.15}$$

or, integrating between limits,

$$\ln \frac{K_{a_2}}{K_{a_1}} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{XI.16}$$

The assumption of constant ΔH is equivalent to assuming that the total heat capacity of the products of the reaction equals that of the initial reactants. This assumption is surprisingly good in a great many cases, and Eqs. (XI.15) and (XI.16) are very useful for correlating and extrapolating experimental data on equilibrium constants.

Equation (XI.15) may also be put in the forms

$$\Delta F^\circ = \Delta H + IT \tag{XI.17}$$

and
$$\Delta F^\circ_{298} = \Delta H_{298} - T\,\Delta S_{298} \tag{XI.17a}$$

In some cases it may be convenient to utilize Eqs. (XI.15) and (XI.17) in the purely empirical forms

$$\log K_a = \frac{A}{T} + B \tag{XI.18}$$

$$\Delta F^\circ = a + bT \tag{XI.19}$$

Any two values of K_a or ΔF° will serve to determine the values of the constants. These two equations are frequently used in place of Eqs. (XI.13) and (XI.14).

Other useful interpolation formulas could be obtained by using other simplified forms of Eq. (IX.101). Thus, if one assumes that ΔH is a linear function of T, one obtains (using empirical coefficients),

$$\log K_a = \frac{A}{T} + B \log T + C \tag{XI.20}$$

Figure XI.2 illustrates the use of a linear $\log K_p$ vs. $1/T$ relationship in the correlation of equilibrium-constant data for the reaction

$$C_2H_4 + H_2O(g) = C_2H_5OH(g).$$
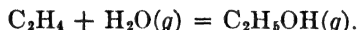
The best straight line (method of averages) representing the data is

$$\log_{10} K_p = \frac{2{,}132}{T} - 6.241$$

The corresponding free-energy equation is

$$\Delta F^\circ = 28.60T - 9{,}740$$

Equation (XI.16) is also useful for a rough estimate of the possibilities of a given reaction for which data are available at 25°C. but not at higher temperatures.
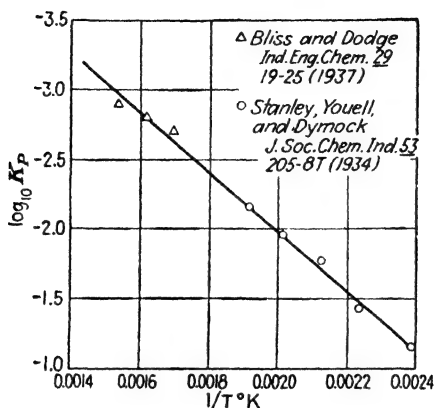
FIG. XI.2.—Correlation of equilibrium constant data.

Illustration 2.—From recent data on heats of formation and on absolute entropy, the standard free-energy change for the reaction $C_2H_4 + H_2O(g) = C_2H_5OH(g)$ at 25°C. is $-2,030$ cal./g-mole $= \Delta F^{\circ}_{298}$.

The heat of reaction at 25°C. $= -11,000$.   Estimate the equilibrium constant for this reaction at 600°K.

From Eq. (IV.245), K_p at 25°C. $= 30.9$

From Eq. (XI.16), $\log \dfrac{K_{p_2}}{30.9} = \dfrac{-11,000}{4.57}\left(\dfrac{1}{298} - \dfrac{1}{600}\right)$

$$K_{p_2} = 2.76 \times 10^{-3}$$

Experimental measurements of this equilibrium give values of K_p of about 2×10^{-3} (see Fig. XI.2).   Using the specific-heat equations given by Parks[1] and Eq. (XI.13), one obtains the value

$$K_{p_2} = 2.36 \times 10^{-3}$$

This method of extrapolating equilibrium-constant values from room temperature to a temperature that might be practicable from a rate stand-point cannot be relied on for accurate values, but frequently an order-of-magnitude value is all that one needs to decide whether a given reaction has possibilities or not.

EFFECT OF PRESSURE

From the general principles of equilibrium it can be deduced that increase in pressure will shift the equilibrium in the direction in which the volume of the system decreases.   Thus in the case of the reaction

$$N_2 + 3H_2 = 2NH_3$$
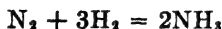
[1] Parks, G. S., *Ind. Eng. Chem.*, **29**, 845–846 (1937).

one can say at once that the formation of NH_3 will be favored by an increase in pressure. Many important organic reactions take place with a decrease in volume and are therefore favored by pressure. This is the basic fact which underlies the recent important developments in high-pressure synthesis.

When it comes to a question of the quantitative effect of pressure, we must distinguish between the effect of pressure on the *equilibrium* and its effect on the *equilibrium constant*. The constants K_a and K_f defined by Eqs. (XI.3) and (IV.247), respectively, are functions of *temperature only*, and hence their value does not change with the pressure. On the other hand, activity or fugacity is affected by the pressure; therefore, any change in pressure must cause a shift in the equilibrium in order that the particular function of activities represented by the equilibrium constant will be unchanged. Even for the special case where $\Sigma n = 0$, as would be the case for the reaction

$$CO + H_2O(g) = CO_2 + H_2$$
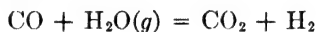
the pressure will still have some effect on the equilibrium. This is not in contradiction to the general principle stated above, for there will be a volume change in the actual system due to deviations from the ideal-gas laws.

An equilibrium constant K_p can be arbitrarily defined for any gaseous system by the equation

$$K_p = \frac{(x_L)^l (x_M)^m \cdots}{(x_A)^a (x_B)^b \cdots} p^{\Sigma n} \qquad \text{(XI.21)}$$

but this constant will be a function of the pressure except for ideal gases. At low pressures where gases approach the ideal state, K_p will be substantially constant and equal to K_f or K_a. Its variation with pressure can be exactly calculated from Eqs. (XI.21) and (XI.3) if the various activities can be expressed as functions of pressure and composition. Data for this purpose are generally lacking, but an approximation can be made by using Eq. (IV.251) in place of Eq. (XI.3), as will be illustrated later (page 494). The best experimental demonstration of the effect of pressure on K_p is given by the equilibrium measurements of Larson and Dodge[1] and of Larson[2] on the ammonia-synthesis reaction. Their results are given in Table XI.1. It may be seen that an increase in pressure from 1 to 1,000 atm. brings about a nearly fourfold increase in K_p.

The application of the exact equation (XI.3) to a gas reaction requires data on the pvT behavior of the system from which the activity may be

[1] Larson, A. T., and R. L. Dodge, *J. Am. Chem. Soc.*, **45**, 2918–2930 (1923).

[2] Larson, A. T., *J. Am. Chem. Soc.*, **46**, 367–372 (1924).

TABLE XI.1.—EFFECT OF PRESSURE ON EQUILIBRIUM CONSTANT FOR THE REACTION
$\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$, AT 450°C.

Pressure, Atm.	$K_p = \dfrac{(x_{NH_3})p^{-1}}{(x_{N_2})^{\frac{1}{2}}(x_{H_2})^{\frac{3}{2}}}$
1	
10	0.00659
30	0.00676
50	0.00690
100	0.00725
300	0.00884
600	0.01294
1,000	0.02328

evaluated. Such data are lacking even for the simplest systems; hence, this equation, though entirely rigorous, is completely unusable—at least for gaseous systems. For a first approximation, one can assume ideal gases and use Eq. (XI.5). A better approximation is obtained by using Eq. (IV.251), which assumes that the gases form an ideal solution though they are not ideal gases.

Illustration 3.—Calculate the equilibrium constant K_p for the ammonia-synthesis reaction at 450°C. and 300 atm. pressure given the value at 1 atm. and the same temperature.

Equation (IV.251) will be assumed to be valid in this case and will be used in the form of Eq. (IV.254). The fugacities of the three gases may be obtained in various ways, as was illustrated in Chap. VI, but we shall use the very simple scheme of the generalized activity-coefficient chart (see Figs. VI.13 and VI.14). The necessary data are given in Table XI.2.

TABLE XI.2.—CRITICAL CONSTANTS OF HYDROGEN, NITROGEN, AND AMMONIA AND
REDUCED VARIABLES FOR 450°C. AND 300 ATM.

Gas	Critical temperature, °K.	Critical pressure, atm.	Reduced temperature*	Reduced pressure*
H_2	33.2	12.8	17.53	14.4
N_2	126.0	33.6	5.73	8.94
NH_3	406	111.6	1.78	2.69

*For H_2, $T_R = T/(T_c + 8)$ and $p_R = p/(p_c + 8)$.

From the figures, $\gamma_{H_2} = 1.09$, $\gamma_{N_2} = 1.14$, and $\gamma_{NH_3} = 0.91$,

$$K_\gamma = \frac{\gamma_{NH_3}}{(\gamma_{N_2})^{\frac{1}{2}}(\gamma_{H_2})^{\frac{3}{2}}} = \frac{0.91}{(1.14)^{\frac{1}{2}}(1.09)^{\frac{3}{2}}} = 0.750$$

The equilibrium constant at 1 atm. has not been measured, but a small extrapolation from the 10-atm. values of Larson and Dodge[1] may be made by using the empirical equation

$$\log_{10} K_p = \frac{2,679.35 + 1.1184p}{T} - (5.8833 + 0.001232p)$$

Loc. cit.

developed by Gillespie[1] to fit the Larson-Dodge data below 100 atm. The value obtained from this equation for 1 atm. and 450°C. is 0.00664.

The observed value of K_p, as calculated by Gillespie[1] from the experimental measurements of Larson,[2] is 0.008770. The calculated value of K_p is obtained as follows:

$$K_p = \frac{K_p{}^\circ}{K_\gamma} = \frac{0.00664}{0.750} = 0.00885$$

$$K_\gamma \text{ (observed)} = \frac{0.00664}{0.00877} = 0.757$$

In Table XI.3 a number of values of K_γ for the ammonia synthesis calculated in the manner just illustrated are compared with the observed values. The latter are obtained from the equations of Gillespie for K_p as a function of pressure and temperature, which smooth the experimental data of Larson and Dodge and Larson.

The agreement up to 600 atm. is very good, and even at 600 atm. it is fair. The marked deviation at 1,000 atm. is probably due to the breakdown of the additive-volume rule upon which Eqs. (IV.251) and (IV.254) are based. Although the rule has been shown to hold quite well for nitrogen-hydrogen mixtures even at 1,000 atm., the presence of ammonia to the extent of nearly 70 mole per cent at this pressure would probably cause a considerable deviation from the rule.

TABLE XI.3.—AGREEMENT BETWEEN OBSERVED AND CALCULATED VALUES OF K_γ FOR AMMONIA SYNTHESIS

Pressure, atm.	K_γ	Temperature, °C.							
		325	350	375	400	425	450	475	500
10	Calculated	0.981	0.983	0.984	0.986	0.987	0.988	0.990	0.992
	Observed	0.986	0.987	0.988	0.990	0 991	0.992	0.993	0.994
30	Calculated	.....	0.960	0.963	0.965	0.967	0.969	0.971	0.973
	Observed	.....	0.963	0.968	0.972	0.974	0.978	0.982	0.985
50	Calculated	.....	0.935	0.942	0.946	0.950	0.953	0.956	0.959
	Observed	.....	0.937	0.946	0.954	0.958	0.965	0 970	0.978
100	Calculated	.....	.....	0.889	0.895	0.900	0.905	0.910	0.914
	Observed	.....	.....	0.894	0.907	0.918	0.929	0.941	0.953
300	Calculated	.....	.....	.....	.....	.....	0.750	0.768	0.788
	Observed	.....	.....	.....	.....	.....	0.757	0.765	0.773
600	Calculated	.....	.....	.....	.....	.....	0.573	0.594	0.612
	Observed	.....	.....	.....	.....	.....	0.512	0.538	0.578
1,000	Calculated	.....	.....	.....	.....	.....	0.443	0.473	0.487
	Observed	.....	.....	.....	.....	.....	0.285	0.334	0.387

[1] GILLESPIE, L. J., *J. Math. Phys. Mass. Inst. Tech.*, **4**, 84–96 (1925).
[2] *Loc. cit.*

The agreement between an observed and calculated mole fraction of ammonia in the equilibrium mixture is better than the agreement between the values of K_γ. For example, at 450°C. and 600 atm. the calculated and observed values for this mole fraction are 0.516 and 0.536, respectively, a difference of only 3.9 per cent compared with 11.9 per cent in the values of K_γ.

That Eq. (IV.251) gives a far better approximation to the facts than the equation (XI.5) based on the assumption of ideal gases is at once apparent from the fact that the values of K_γ would all be 1.0 on the basis of the latter equation.
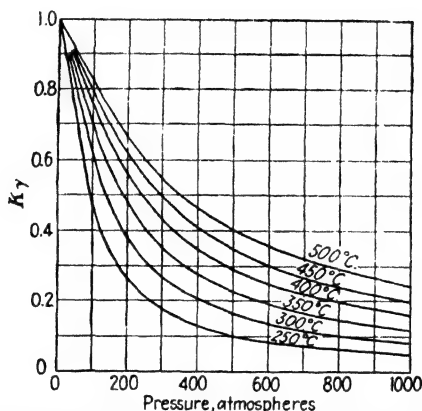
Fig. XI.3.—Values of K_γ for the methanol-synthesis reaction.

In some cases the effect of pressure on the equilibrium constant K_p is slight even though the gases deviate greatly from ideality. For example, this is apparently true for the reaction

$$C_2H_4 + H_2O(g) = C_2H_5OH(g)$$
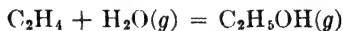
if we accept Eqs. (IV.251) and (IV.254) as being applicable. In this case, the deviations from ideality compensate one another so that K_γ is substantially equal to 1.0 at high pressures.

This method of estimating the effect of pressure on the equilibrium constant is particularly useful in the case of organic reactions where pvT data are generally lacking even for the individual components. On the other hand, if the critical constants are known, the fugacities can be obtained from the generalized chart and K_γ calculated. In Fig. XI.3 are shown K_γ values for the reaction

$$CO + 2H_2 = CH_3OH$$
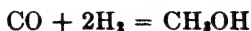
obtained in this way.[1]   The extent of departure from an ideal-gas equilibrium is very marked in this case.

PREDICTION OF EQUILIBRIUM CONSTANTS FROM THERMAL DATA

The experimental measurement of equilibrium constants is a time-consuming and often a difficult task.   Hence, a means of predicting them is desirable.   There are many reactions, especially in the organic field, that are difficult to carry out in practice.   Before embarking on a long and expensive experimental program to investigate catalysts and other conditions necessary to cause reaction, it is desirable to have some assurance that the equilibrium is favorable, in other words, that reaction to the desired extent is thermodynamically possible.   Much effort has been wasted in the past in the search for catalysts or other means of hastening reactions that could have been shown, on thermodynamic grounds, to be incapable of proceeding very far in the direction desired. A prediction, in which confidence could be placed, of the equilibrium constant in the methanol-synthesis reaction would have been of great economic value prior to 1923.

Feasibility of a Reaction.—The remark is sometimes made that a given reaction is "thermodynamically impossible." This is a loose statement that has no meaning in the absence of qualifying statements. For example, any reaction, starting with pure reactants uncontaminated by any of the products, will have a tendency to proceed to some extent, though this may be only infinitesimal.   Thus the reaction

$$H_2O(g) = H_2 + \tfrac{1}{2}O_2$$
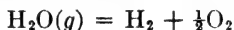
proceeds to some extent at 25°C.; we can even calculate with considerable assurance the percentage of water vapor that would be decomposed. From the accurately known value for $\Delta F°$ of this reaction at 25°C., the equilibrium constant is about 1×10^{-40} and the extent of decomposition is infinitesimally small but definite.

From the value of the standard free-energy change for any reaction, we can form an opinion about the feasibility of the reaction without further calculation.   Thus if $\Delta F° = 0$ at a given temperature, then $K_a = 1$ and it is obvious that the reaction must proceed to a considerable extent before equilibrium is reached.   The situation becomes less favorable as $\Delta F°$ increases in the positive direction, but there is no definite value that one can choose as clearly indicating that the reaction is not feasible from the standpoint of industrial operation.   At 600°K., the $\Delta F°$ for the methanol-synthesis reaction is $+11,000$, and yet the reaction is certainly feasible at this temperature.   In this case, the unfavorable free-energy change for the standard state is partly overcome by

[1] Newton, R. H., and B. F. Dodge, *Ind. Eng. Chem.*, **27**, 577–581 (1935).

utilizing high pressure to displace the equilibrium. Other means can also be used for this purpose, such as changing the ratio of reactants or removing one of the reaction products.

For the purpose of ascertaining quickly and only approximately if any given reaction is promising at a given temperature, the following guide may be useful:

$\Delta F° < 0$. Reaction is promising.

$\Delta F° > 0$ but $< +10,000$. Reaction is of doubtful promise but warrants further study.

$\Delta F° > +10,000$. Very unfavorable. Would be feasible only under unusual circumstances.

It should be understood that these are only approximate criteria that are useful in preliminary exploratory work.

Addition of ΔF Values.—Free-energy changes and hence equilibrium constants can be obtained by the addition of the values for reactions whose algebraic sum is the reaction in question. The fundamental basis for this is the fact that ΔF depends only on initial and final states and not on the intermediate steps by which the final state is reached. For example, the reaction

$$C + \tfrac{1}{2}O_2 = CO \qquad\qquad (XI.22)$$

can be regarded as composed of the following steps:

$$C + CO_2 = 2CO \qquad\qquad (XI.23)$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O(l) \qquad\qquad (XI.24)$$
$$CO + H_2O(l) = CO_2 + H_2 \qquad\qquad (XI.25)$$
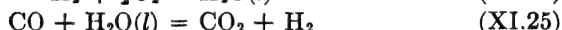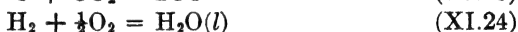
Adding equations, $(XI.23) + (XI.24) + (XI.25) = (XI.22)$
   $\therefore \Delta F° (XI.22) = \Delta F° (XI.23) + \Delta F° (XI.24) + \Delta F° (XI.25)$

For this to be true, one must be careful to see that all substances which appear in more than one equation are in the same state. In other words, they must be at the same temperature, pressure, and state of aggregation; otherwise, their free energies will not cancel.

The simplest way to obtain the free-energy change for any reaction is by algebraic combination of the free energies of formation of the various substances concerned. Thus, for the reaction

$$CO + 3H_2 = CH_4 + H_2O(g)$$
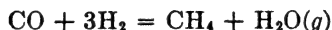
ΔF (reaction) $= \Delta F$ (formation of CH_4) $+ \Delta F$ (formation of gaseous H_2O)
$\qquad\qquad\qquad\qquad\qquad\qquad - \Delta F$ (formation of CO).

Since H_2 is an element and not a compound, its ΔF of formation is zero. The free energy of formation of any compound is simply the free-energy change for the reaction by which the compound is formed from the elements. For example, the free energy of formation of liquid methanol

is the free-energy change for the reaction

$$C + \tfrac{1}{2}O_2 + 2H_2 = CH_3OH(l)$$

Free energies of formation are generally given for the case where all substances involved are in standard states at 25°C. If one had a table of the free energies of formation at 25°C. of all the compounds involved in any set of reactions in which he was interested, it would be a simple matter of addition to find the ΔF for any given reaction. Then with the aid of specific-heat data one can find the ΔF at any temperature by means of Eq. (XI.14) and finally the equilibrium constant by Eq. (IV.245). The chief obstacle that prevents the universal use of these simple methods is the lack of the necessary data. It will be a long time before workers in this field are able to assemble enough data to enable one to predict equilibria in any large number of cases.

$\Delta F°$ **of Formation of Organic Compounds from Considerations of Structure.**—The task of obtaining values for the standard free energy of formation of organic compounds would be greatly simplified if structural relationships were developed that would permit the prediction of many $\Delta F°$ values from a few measured ones. A very small but significant amount of progress in this direction has been made. For example, Ewell,[1] after making a critical review of the existing data on $\Delta H°$ and $\Delta S°$ for paraffin and olefin hydrocarbons, developed certain simple rules for estimating $\Delta H°_{298}$ and $S°_{298}$ for branched-chain paraffins, for 1-olefins, and for branched and nonterminal olefins from the known values for the normal gaseous paraffins of the same number of carbon atoms. The rules consist merely in the addition of certain fixed quantities depending on the type of structural change. Such generalizations are admittedly rough but are of some utility in the absence of experimental data. They have been applied in the prediction of yields from hydrocarbon reactions of considerable industrial importance such as isomerization, polymerization, and alkylation reactions.

The Third Law of Thermodynamics.—This law was briefly referred to in earlier chapters, but discussion of it was deferred until we were ready to make some use of it. As a matter of fact, our use of it will be quite indirect and hence we shall limit our discussion to a few of the salient points.

The Nernst heat theorem, from which the third law developed, was the culmination of a long series of attempts by chemists to calculate equilibrium points in chemical reactions from thermal data. In Chap. III it was shown that this question is related to the entropy change at absolute zero. From the trend of values of ΔF and ΔH with temperature

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[1] EWELL, R. H., *Ind. Eng. Chem.*, **32**, 778 (1940).

at temperatures far removed from absolute zero, Nernst made a brilliant "guess" about the trend as T approaches zero. His assumption is equivalent to writing

$$\Delta S \text{ and } \Delta C_p = 0 \qquad \text{at} \qquad T = 0$$

where the Δ refers to any physical change or chemical reaction. If all substances have the same entropy and specific heat at $T = 0$, it is only reasonable that these values must be zero. This was the assumption of Planck which has since become almost universally accepted as the third law. Since C_p is necessarily zero if $S = 0$, it is sufficient to state that the entropy of individual phases is equal to zero at abolute zero.

This statement of the law is too general and requires some further restriction because there are cases where the entropy is greater than zero at $T = 0$. From the statistical standpoint, the entropy will be zero only if the substance is in stable equilibrium at all stages of the cooling process and ultimately approaches $T = 0$, with all particles of which the substance is composed at their lowest energy levels. Planck expressed this idea in the equation

$$S = R \ln g$$

where g represents the number of configurations in which the system can exist. For the single state of lowest energy, $g = 1$ and $S = 0$. If the system has not been brought to this equilibrium state at $T = 0$, it will have a positive entropy due to the multiplicity of configurations. Thus we should expect that all liquids (except helium) since they exist in an unstable, supercooled state (like glass at ordinary temperature) would have a positive entropy, and this has been verified by experiment. Likewise solutions should have an entropy of mixing, and there is experimental confirmation of this. In the case of some gases such as H_2, CO, N_2O, H_2O, and a few others, discrepancies between absolute entropies calculated from spectroscopic data and those measured calorimetrically have led to a recognition of the existence of a certain "multiplicity" of configuration in some molecules which is "frozen" at the low temperatures so that the single equilibrium configuration of least energy cannot be attained and the calorimetric entropy will be too low. This is particularly shown in the case of hydrogen, which has two different forms of the molecule, the para and ortho forms, owing to a difference in nuclear spin. When hydrogen is cooled to low temperatures, the crystals obtained are a solid solution of the two forms, and change to the stable para form does not occur. It has been shown that the difference of 4.39 entropy units must be added to the calorimetric entropy to obtain the true absolute entropy. However, it has also been shown that

nuclear spin entropies cancel in reactions at ordinary and higher temperature levels, and the correct entropy to use in equilibrium calculations is the so-called "practical" entropy, which is the spectroscopic entropy corrected for the entropy associated with nuclear spin at elevated temperatures. Since many elements consist of a mixture of isotopes, they will possess an entropy of mixing at $T = 0$ owing to this fact, but this can be disregarded in any practical application because the proportions of the isotopes are not changed either by ordinary physical changes or by chemical reaction.

It is to be noted that, whereas the first two laws led to the definition of new quantities of fundamental importance—the first law to the concept of energy and the second to thermodynamic temperature and entropy—the third law introduces no new quantity but merely places a limitation on the value of one of the previous ones. For this reason, some authors prefer not to elevate the fact of absolute entropy to the dignity of a "law" on a par with the other two.

Experimental verification of the third law consists in predicting chemical equilibria from the use of absolute entropies calculated from either calorimetric or spectroscopic data and comparing the prediction with experimentally determined equilibria. Also the comparison of absolute entropies obtained in the two ways, *i.e.*, spectroscopic and thermal, is a means of verification. It can be stated briefly that, in the case of all reactions that have been studied in condensed systems, the third law is verified within the experimental error. In the case of gas reactions or in the comparison of the entropies from the two different sources, there are certain discrepancies, but for the most part these have been satisfactorily accounted for along the lines suggested above. As far as practical application is concerned, we may conclude with confidence that all chemical individuals possess a practical value of absolute entropy that can be used in the prediction of equilibria. For relatively simple molecules, this entropy can be calculated from spectroscopic data with the aid of quantum statistical mechanics, and values so obtained are probably more accurate than those obtained from thermal measurements. For most substances the calorimetric method must be used, and this consists in the determination of all sensible and latent heats evolved from the substance as it is cooled. It is not practicable to cool to absolute zero, but if the cooling is carried out with liquid hydrogen to about 12°K., the remaining entropy is small, and extrapolation to $T = 0$ can be made with reasonable confidence. One method for doing this was suggested in Chap. IX. The final result of such measurements is a table of absolute entropies of elements, ions, and compounds. Such tables are still far from complete, but values for many substances of industrial importance are available.

In this brief review of the third law, only a few "high lights" could be brought out. For further details the reader is referred to an excellent review by Eastman.[1]

Application of the Third Law.—Ultimately all values of free energy of reaction go back either to equilibrium measurements or to the equation

$$\Delta F = \Delta H - T \Delta S \tag{XI.26}$$

This equation combined with the third law of thermodynamics, which permits the evaluation of absolute entropies, enables one to predict equilibria from purely thermal measurements. This is an extremely important equation, and its application will be illustrated in some detail by numerical examples.

The minimum amount of data necessary to predict the equilibrium constant K_a, for a gas-phase reaction at any temperature, is as follows:

1. Absolute entropy of each substance at a given standard temperature and in its standard state.

2. Heat of reaction at a standard temperature.

3. Specific heat of each substance over the range from the standard temperature to the temperature in question.

4. Latent heat of vaporization and vapor pressure of substances whose state is that of a liquid or solid at the standard temperature.

Other equivalent data might be used. For example, instead of using the absolute entropy of each substance, one could just as well use the entropies of formation of all the reacting constituents. The entropy of formation is obtained by combination of the absolute entropy of the compound and the entropies of the respective elements. The heat of reaction may be obtained from the heats of formation, which, in turn, are usually obtained (for an organic reaction, at least) from the heats of combustion of the compound and the elements composing it.

For reactions involving the liquid phase, additional data are generally needed to relate equilibrium concentrations in the vapor and liquid phases. In the case of reactions at elevated pressures, data on the compressibilities would be needed if K_p rather than K_a were desired (K_a is independent of pressure) or if concentrations were to be calculated from a value of K_a.

Illustration 4.—What is the equilibrium constant K_p for the methanol-synthesis reaction

$$CO + 2H_2 = CH_3OH(g) \tag{1}$$

as a function of temperature at a pressure of 1 atm. as predicted from thermal data?

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[1] EASTMAN, E. D., *Chem. Revs.*, **18**, 257 (1936).

Direct application of Eq. (XI.26) can be made at 25°C., using suitable values for the heats of formation of gaseous CH_3OH and of CO and knowing the absolute entropies of CO, H_2, and CH_3OH. The following entropy data will be used:

S of liquid CH_3OH at 25°C. = 30.3 g.-cal./g.-mole/°K.*
S of CO at 25°C. and 1 atm. = 47.3 g.-cal./g.-mole/°K.†
S of H_2 at 25°C. and 1 atm. = 31.25 g.-cal./g.-mole/°K.‡

The entropy of CH_3OH is based on specific-heat and latent-heat measurements, whereas the entropies of CO and H_2 were deduced from spectroscopic measurements. The ΔH for reaction (1) is obtained from a combination of ΔH's for the following reactions:

$$CH_3OH(l) + 1\tfrac{1}{2}O_2 = CO_2 + 2H_2O(l) \tag{2}$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O(l) \tag{3}$$
$$CO + \tfrac{1}{2}O_2 = CO_2 \tag{4}$$
$$CH_3OH(l) = CH_3OH\ (g,\ 0.163\ atm.) \tag{5}$$
$$CH_3OH\ (g,\ 1\ atm.) = CH_3OH\ (g,\ 0.163\ atm.) \tag{6}$$
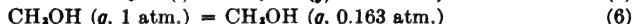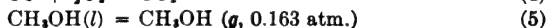
(0.163 atm. is the vapor pressure of CH_3OH at 25°C.)

$$\Delta H_1 = 2\,\Delta H_3 + \Delta H_4 - \Delta H_2 + \Delta H_5 - \Delta H_6 \tag{7}$$

The following values of ΔH in gram-calories per gram-mole for 25°C. are available:[1]

$$\Delta H_3 = -68,313\S$$
$$\Delta H_4 = -67,623\|$$
$$\Delta H_2 = -173,630\P$$
$$\Delta H_5 = 8930**$$

ΔH_6 will be assumed negligible. It would be zero for an ideal gas, and the error in assuming that methanol vapor is ideal at these low pressures is probably very small.

$$\Delta H_1 \text{ by (7)} = -21,690$$

ΔS of vaporization of CH_3OH at 0.163 atm. $= \dfrac{8,930}{298.1} = 30.0$

ΔS for $CH_3OH\ (g,\ 0.163\ atm.) \rightarrow CH_3OH\ (g,\ 1\ atm.) = R \ln \dfrac{0.163}{1} = -3.60$

S of CH_3OH vapor at 1 atm. $= 30.3 + 30.0 - 3.60 = 56.7$
$$\Delta S_1 = 56.7 - 47.3 - 62.5 = -53.1$$
Finally, $\quad \Delta F_1 = -21,690 - 298\,(-53.1) = -5,850$

* KELLEY, K. K., *J. Am. Chem. Soc.*, **51**, 180–187 (1929).

† CLAYTON, J. O., and W. F. GIAUQUE, *Ibid.*, **54**, 2610–2626 (1932); **55**, 5071–5073 (1933).

‡ KELLEY, K. K., *Ind. Eng. Chem.*, **21**, 353–354 (1929).

[1] More recent thermal data have become available since this problem was first solved, but the use of these data changes the solution only to small extent, and it was not considered necessary to make the revision.

§ ROSSINI, F. D., *Bur. Standards J. Research*, **6**, 1–35 (1931).

‖ ROSSINI, F. D., *Bur. Standards J. Research*, **6**, 37–49 (1931).

¶ ROSSINI, F. D., *Bur. Standards J. Research*, **8**, 119–39 (1932).

** FIOCK, E. F., D. C. GINNINGS, and W. B. HOLTON, *Bur. Standards J. Research*, **6**, 881–900 (1931).

One objection that might be raised to this calculation is that methanol vapor cannot exist in stable equilibrium at 25°C. and 1 atm. and therefore the standard state chosen for methanol is a purely hypothetical one. This is a valid objection. We might have avoided this use of a hypothetical state either by taking as our reference temperature a temperature equal to or greater than the normal boiling point of methanol or by choosing a lower pressure, say 0.1 atm., for our standard state of pressure. It is very convenient to refer all thermodynamic data to the reference state of 25°C. and 1 atm. pressure instead of having several different reference states, and it is believed that the slight extrapolation into an unstable region which this necessitates in a case like the one we are now considering introduces a negligible error. In other words, although it is incorrect in principle to use a hypothetical state in this way, it may be justified on the grounds of expediency.

For molal heat capacities at constant pressure we shall use the equations already given on page 490, from which $\Delta H_0 = -17,530$.

Substituting values in Eq. (XI.14),

$$\Delta F^\circ = -17,5\smile + 18.19T \ln T - 0.0141T^2 + IT$$

From
$$\Delta F^\circ_{298} = -5850, \qquad I = -60.4$$

Finally,

$$\log_{10} K_p{}^\circ = \log_{10} K_f = \frac{3,835}{T} - 9.150 \log_{10} T + 0.00308T + 13.20 \qquad (8)$$

At 250°C. $(T = 523)$ this equation gives $K_p{}^\circ = 2.0 \times 10^{-3}$. This may be compared with the experimental value of 2.3×10^{-3} obtained by Newton and Dodge.[1] The agreement is unusually good for data in this general field.

It is of interest to compare this result with that obtained from the approximate equation (XI.16). Using for ΔH the value at 25°C., we have

$$\log_{10} \frac{K_{p_2}}{20,000} = -\frac{21,690}{4.571}\left(\frac{1}{298} - \frac{1}{523}\right)$$

or
$$K_{p_2} = 2.76 \times 10^{-3}$$

The agreement between the approximate and the more exact method is relatively good in this case and probably better than one could expect it to be in general.

This procedure for the prediction of equilibrium constants from thermal data is a valuable tool in the hands of the research man; but, in the majority of the cases at the present time, accurate data are lacking, and one cannot expect more than order-of-magnitude results. Since, as the above illustration shows, the free-energy change of the reaction is apt to be small relative to some of the thermal quantities involved, a small percentage error in one of the latter quantities produces a much greater percentage error in the ΔF of the reaction and a still greater one in K_p. Referring again to Illustration 4, a 1 per cent change in the heat of combustion of methanol, everything else remaining the same, would change the K_p at 250°C. to 1.07×10^{-2}, or nearly fivefold.

At one time the predicted equilibrium constants for the methanol-synthesis reaction at about 600°K. were anywhere from 10 to 200 times the best experimental values. This discrepancy remained a mystery

[1] Newton, R. H., and B. F. Dodge, *J. Am. Chem. Soc.*, **56**, 1287–1291 (1934).

for some time until it was suggested[1] that inaccuracies in the thermal data, especially the heat of combustion of methanol, could easily account for much of the difference. This was confirmed when the heat of combustion was redetermined by Rossini.[2] At the present time, there is good agreement between the experimental and the predicted equilibrium constants for this reaction.

As was pointed out in Chap. IX in connection with the discussion of heat of reaction, the errors are enormously magnified in the case of such reactions as the isomerization of hydrocarbons where the ΔH of reaction is a very small fraction of the ΔH of combustion. In these cases, thermal data of the very highest accuracy are necessary even for rough predictions of equilibria.

The prediction of equilibrium constants from thermal data by the method outlined has been checked against .perimental determinations in enough cases so that we can be reasonably , ell assured that the method is reliable if accurate thermal data are available.

For a recent application of the third law to the calculation of the free energy change of a chemical reaction and a discussion of the calculation of enthalpies and free energies from spectroscopic data by statistical mechanics, reference may be made to a paper by Aston.[3]

We shall now furnish another illustration, which will involve the presence of a liquid as well as a gaseous phase and the use of different standard states.

Illustration 5.—Calculate from thermal data the equilibrium constant for the reaction between ethylene gas and water to form ethyl alcohol at 254°C. (527°K.), the pressure being high enough so that a liquid phase is present.

All three constituents will, of course, be present in both the gas and liquid phases and there will be three simultaneous equilibria in the system, (1) chemical equilibrium in the liquid phase, (2) chemical equilibrium in the gas phase, and (3) phase equilibrium. Either we can treat the chemical equilibrium in the liquid phase directly, or we can regard it as a combination of the other two equilibria and treat it as if the reaction occurred wholly in the gas phase. Since the free-energy change for any reaction is entirely independent of the mechanism or steps of the reaction, there is no real difference between these methods.

Let us write the reaction in the form

$$C_2H_4(g) + H_2O(l) = C_2H_5OH(l)$$
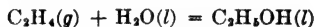
In order to obtain the equilibrium constant defined by the equation

$$K_a = \frac{a_C}{(a_A)(a_B)}$$

where a_A, a_B, and a_C are activities of ethylene, water, and ethanol, respectively, one

[1] DODGE, B. F., *Ind. Eng. Chem.*, **22**, 89–90 (1930).

[2] ROSSINI, F. D., *Proc. Nat. Acad. Sci.*, **17**, 343–347 (1931).

[3] ASTON, J. G., *Ind. Eng. Chem.*, **34**, 514 (1942).

must find the free-energy change for the reaction with each constituent in a standard state (unit activity). The reaction as written above implies that the standard states chosen are as follows:

Ethylene as pure gas at a pressure of 1 atm. (more strictly, fugacity = 1 atm.).

Water as the pure liquid at 1 atm.

Ethanol as the pure liquid at 1 atm.

Throughout the discussion the temperature is assumed to be 25°C. unless otherwise noted.

ΔH for reaction (1) may be obtained by combination of data for the following reactions:
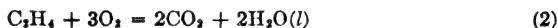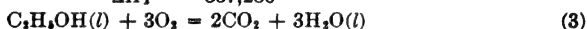
$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O(l) \qquad (2)$$
$$\Delta H_2 = -337,280^*$$
$$C_2H_5OH(l) + 3O_2 = 2CO_2 + 3H_2O(l) \qquad (3)$$
$$\Delta H_3 = -326,660\dagger$$
$$\Delta H_1 = \Delta H_2 - \Delta H_3 = -10,620$$

ΔS for reaction (1) is obtained from the following data:

Entropy of liquid $C_2H_5OH = 38.40\ddagger$

Entropy of gaseous H_2O at 1 atm. $= 45.10\S$

Heat of vaporization of H_2O at 25°C. $= 10,500\|$.

Vapor pressure of H_2O at 25°C. $= 0.0312$ atm.

$$\therefore \text{ Entropy of liquid } H_2O = 45.10 - 4.57 \log \frac{1}{0.0312} - \frac{10,500}{298.2} = 16.8$$

Entropy of $C_2H_4 = 52.3\P$

$$\Delta S \text{ for reaction } (1) = 38.40 - 16.8 - 52.3 = -30.7$$
$$\Delta F° \text{ for reaction } (1) = -10,620 + 30.7 \times 298.2 = -1,470$$

Since

$$\log_{10} K_a = \frac{-\Delta F°}{4.57T}$$

at $T = 298$,

$$K_a = 12.0$$

For an approximate estimation of K_a at 527°K., we shall assume that ΔH is a constant and use the relation

$$\log K_a = \frac{-\Delta H}{4.57T} + C$$

From the value of K_a at 298, $C = -6.72$. At 527°K.,

$$K_a = 5.0 \times 10^{-3}$$

Presumably a more accurate value of K_a at 527°K. could be obtained if specific-heat data were available to enable one to relate ΔH to the temperature. There are, however, certain difficulties involved in getting K_a for this reaction at the temperature we have chosen that should be discussed in more detail because they have an important bearing on the general question of a choice of a standard state. In the first place, the critical temperature of ethanol is below 527°K., and therefore the standard state

* ROSSINI, F. D., and J. W. KNOWLTON, *Bur. Standards J. Research*, **17**, 635–638 (1936).

† ROSSINI, F. D., *Bur. Standards J. Research*, **13**, 189–202 (1934).

‡ KELLEY, K. K., *J. Am. Chem. Soc.*, **51**, 779–786 (1929).

§ GORDON, A. R., *J. Chem. Phys.*, **2**, 65–72 (1934).

‖ GIAUQUE, W. F., and J. W. STOUT, *J. Am. Chem. Soc.*, **58**, 1144–1150 (1936).

¶ PARKS, G. S., *Chem. Revs.*, **18**, 325–334 (1936).

chosen for it at this temperature is a hypothetical one, as ethanol cannot exist as a liquid at 527°K.

In the present case there is the additional difficulty, when one tries to relate ΔH to the temperature, of knowing what value to use for C_p. The specific heat C_p of all fluids becomes infinite at the critical point.

Even if the temperature at which K_a is desired were below the critical temperature, the standard state would still be an unstable state because ethanol and water do not exist in stable equilibrium as liquids at 1 atm. and elevated temperatures. One could get around this by choosing the standard at such a pressure that both these substances would be liquid at the temperature concerned. From a practical standpoint this may be an unnecessary refinement because the effect of pressure on the free energy of liquids is relatively small. Thus, for the change

$$C_2H_5OH \ (l, \ 1 \ \text{atm.}) \ = \ C_2H_5OH \ (l, \ 100 \ \text{atm.})$$
$$\Delta F \ = \ \int v \ dp$$
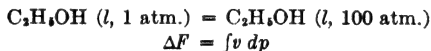
Assuming the volume to be independent of pressure,

$$\Delta F \ = \ v \ \Delta p$$
At 25°C., $\qquad\qquad v \ = \ 57.5 \ \text{cc./g.-mole}$
$$\Delta F \ = \ 57.7 \times 99 \ = \ 5,693 \ \text{cc.-atm.}$$
$$= \ 138 \ \text{g.-cal.}$$

Although this is an appreciable fraction of the ΔF calculated for the reaction, it is probably well within the experimental error of some of the thermal quantities involved in the calculation of ΔF.

Furthermore, in order to make use of the equilibrium constant to calculate equilibrium conditions, data on the vapor pressure of ethanol over solutions ranging from nearly pure ethanol down to the equilibrium concentration, which might be quite dilute, would be required.

These difficulties are avoided or at least rendered less severe if one chooses a different standard state for the ethanol, *viz.*, that of a dilute solution. On this basis, (1) would become

$$C_2H_4(g) \ + \ H_2O(l) \ = \ C_2H_5OH(aq) \qquad\qquad (4)$$
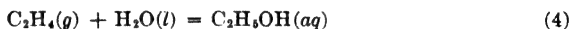
ΔF for this reaction is the sum of ΔF for reaction (1) and that for the reaction

$$C_2H_5OH(l) \ = \ C_2H_5OH(aq) \qquad\qquad (5)$$
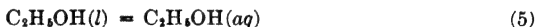
ΔF for process (5) is readily obtained by imagining it to take place isothermally and reversibly in the following steps:

1. Vaporization of ethanol at its vapor pressure p_C.
2. Isothermal expansion of ethanol vapor from p_C to its partial pressure $\bar{p}_C$ over an aqueous solution.
3. Condensation of the vapor through a semi-permeable membrane between the vapor and the solution so that the condensation occurs at equilibrium at the pressure $\bar{p}_C$.

Steps 1 and 3 involve no change in F. For step 2, assuming the vapor is an ideal gas,

$$\Delta F \ = \ RT \ln \frac{\bar{p}_C}{p_C}$$

and this must also be the ΔF for reaction (5). Following the usual practice, we take a 1M solution as the standard state. From such a solution (mole fraction EtOH = 0.0177) the partial pressure $\bar{p}_C$ is 3.65 mm,

$$p_C = 59.0 \text{ mm.}$$

$$\therefore \Delta F = RT \ln \frac{3.65}{59.0} = -1,650$$

Finally, ΔF for reaction (4) $= -1,470 - 1,650 = -3,120$

K_a at 298°K. $= 195$. ΔH for (5) will be approximately equal to the heat of solution of 1 mole of C_2H_5OH in water to form an infinitely dilute solution, or $-2,500$ cal. Then $\Delta H_4 = -13,100$. Assuming this to be a constant, K_a at 527°K. for (4) $= 0.014$.

Experimental results on liquid-phase equilibrium for this reaction are meager and not very concordant, but the results of Gilliland, Gunness, and Bowles[1] may serve as a rough check on the order of magnitude of the calculated constant. From their four runs at 527°K., we can calculate K_a on the basis of the following assumptions:

1. The ethanol concentration is small, and Henry's law can be assumed for the liquid phase. Since the standard state is a 1-M. solution, $a_{EtOH} = m_{EtOH}$.

2. Since the mole fraction of H_2O is about 0.9, Raoult's law can be assumed and $a_{H_2O} = x_{H_2O}$.

3. The vapor can be considered an ideal solution, and $\bar{f} = yf$ where f, the fugacity of pure C_2H_4 at the given temperature and total pressure, is to be obtained from the generalized activity-coefficient chart.

The results of our calculations are as follows:

Run No.	Total pressure, atm.	Mole fraction in liquid		Mole fraction of C_2H_4 in vapor	Activities			K_a
		EtOH	H₂O		EtOH	C₂H₄	H₂O	
7	82.6	0.014	0.956	0.475	0.813	37.3	0.956	0.0228
8	196.9	0.060	0.918	0.380	3.63	67.3	0.918	0.0589
9	264.2	0.084	0.881	0.250	5.29	59.1	0.881	0.101
10	129.7	0.0445	0.937	0.226	2.63	27.3	0.937	0.103

Mean $K_a = 0.071$.

The agreement between the calculated K_a and these experimental values is as good as could be expected considering the assumption of a constant ΔH and in view of the fact that the experimental values themselves are not very concordant.

Illustration 6.—Calculate from thermal data the equilibrium constant K_a for the synthesis of formic acid from CO and water in the presence of a liquid phase at 156°C., based on the following standard states:

For CO, gas at 1 atm.

For H_2O, pure liquid.

For formic acid, a 1 molal aqueous solution.

We have chosen to give this additional illustration because it involves a factor that did not enter into the previous one, viz., a polymerization of the vapor. The reaction to be considered is

$$CO + H_2O(l) = HCOOH(aq) \qquad (1)$$

ΔF_{298} for the reaction $\qquad CO + H_2O(l) = HCOOH(l) \qquad (2)$
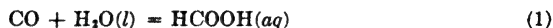
[1] GILLILAND, E. R., R. C. GUNNESS, and V. O. BOWLES, *Ind. Eng. Chem.*, **28**, 370–372 (1936).

is obtained from the free energies of formation of each pure component based on the third law, which are as follows:

$$\Delta F_{298} \text{ for formation of CO} = -32,700 \text{ g.-cal./g. mole}$$
$$\Delta F_{298} \text{ for formation of } H_2O \text{ } (l) = -56,560$$
$$\Delta F_{298} \text{ for formation of HCOOH } (l) = -85,300$$

ΔF_{298} for reaction (2) = 3,960.

To get to reaction (1) there is required the free-energy change for

$$HCOOH(l) = HCOOH(aq) \tag{3}$$
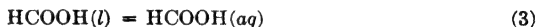
and this can be obtained from data on the vapor pressures of pure formic acid and its aqueous solutions, allowance being made for the following equilibrium, which exists in the vapor,

$$(HCOOH)_2 = 2HCOOH \tag{4}$$

Ramsperger and Porter[1] investigated this equilibrium at 25°C. and found the partial pressure of monomolecular vapor over the pure liquid and over a 1-M. aqueous solution to be 1.17×10^{-2} atm. and 7.89×10^{-5} atm. respectively. According to them $\Delta \mu$ for (3) is

$$RT \ln \frac{7.89 \times 10^{-5}}{1.17 \times 10^{-2}} = -2,960$$

$\therefore \Delta\mu$ for (1) is $3,960 - 2,960 = 1,000$

$$\Delta H \text{ for (1)} = -4,920$$

which is obtained from the following values:

$$\Delta H \text{ of formation of liquid formic acid} = -99,750$$
$$\Delta H \text{ of formation of liquid } H_2O = -68,310$$
$$\Delta H \text{ of formation of CO} = -26,617$$
$$\Delta H \text{ of solution of HCOOH} = -100$$

Assuming ΔH to be constant, K_a at 156°C. $= 1.45 \times 10^{-2}$. Branch[2] investigated this reaction experimentally, and his results lead to a K_a of 1.18×10^{-2} at 156°C. This is excellent agreement, especially when one realizes that an error of only 0.17 per cent in the ΔF of formation of HCOOH would account for the difference.

When the equilibrium constant is desired for a vapor-phase reaction between substances some of which are normally liquids at the standard reference temperature of 25°C., data on the latent heats of vaporization at 25°C. are needed for a rigorous calculation. Such data are generally not available; but one can calculate the latent heat from vapor-pressure data by the methods illustrated in Chap. VI, or one may estimate it approximately by one of the methods illustrated in Chap. IX. In many cases it will be sufficiently accurate to assume the latent heat at 25°C. to be the same as that at the normal boiling point, which is more generally available. It frequently happens that one is not justified in spending

[1] RAMSPERGER, H. C., and C. W. PORTER, *J. Am. Chem. Soc.*, **48**, 1267–1273 (1926); **50**, 3036–3038 (1928).

[2] BRANCH, G. E. K., *J. Am. Chem. Soc.*, **37**, 2316–2326 (1915).

time to obtain an accurate value because an approximate one will serve the purpose just as well.   In fact, when calculating an equilibrium constant, one should always keep in mind the use to which it is to be put; this may often save spending a great deal of time on unnecessary refinements.   The following will illustrate some of these points.

Illustration 7.—It is desired to estimate the equilibrium constant for the reaction $C_2H_4 + C_6H_6(g) = C_2H_5C_6H_5(g)$ in order to determine if the reaction in the gas phase is feasible under reasonable conditions.

The following data are taken from various sources:

Substance	ΔF_{298}	ΔH_{298}
Ethyl benzene (l)..........................	26,300	−5,070
Benzene (l).............................	29,400	11,630
Ethylene (g)............................	15,820	11,975

The latent heats of vaporization can be estimated by several of the methods given in Chap. IX.   Using the Kistiakowsky equation

$$\frac{L}{T_B} = 8.75 + 4.575 \log_{10} T_B$$

the following values are obtained:

Substance	Normal boiling point T_B, °K.	Molal latent heat of vaporization
Benzene..............	353.2	7,200
Ethyl benzene.......	408	8,450

To get the latent heat at 25°C., the method of Watson[1] will be used.   This requires a knowledge of the critical temperatures as well as a value at some one temperature. For benzene, $T_c = 561.6$°K.   For ethyl benzene, T_c was estimated by the method of Watson[2] to be 624°K.

Estimated L at 25°C. = 9,800 for ethyl benzene and 8,000 for benzene.[3]

Vapor pressure of benzene at 25°C. = 0.1235 atm.

Vapor-pressure data on PhEt are very meager and not consistent but from the data in International Critical Tables the vapor pressure at 25° is estimated to be about 20 mm.

For the change,
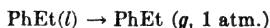
$$\text{PhEt}(l) \rightarrow \text{PhEt }(g, 1 \text{ atm.})$$
$$\Delta F_{298} = RT \ln \tfrac{760}{20} = 2,160 \text{ cal./mole}$$
$$\Delta F_{298} \text{ of formation of PhEt}(g) = 28,460$$

[1] WATSON, K. M., *Ind. Eng. Chem.*, **23**, 360–364 (1931).

[2] *Ibid.*

[3] KOLOSOVSKII, N. A., and I. S. MEZHENIN [*Bull. Soc. Chim.*, **49**, 1461–1465 (1931)] give 9,900 as the latent heat of vaporization of PhEt at 26°C.   Fiock, Ginnings, and Holton (*op. cit.*) give 8,050 for benzene.

Similarly, ΔF_{298} for C_6H_6 = 30,640

Finally, ΔF_{298} for the reaction in question = 28,460 − 15,820 − 30,640 = −18,000

$$\ln K_p = \frac{-\Delta F^\circ}{RT}$$

$$K_p = 1.6 \times 10^{13}$$

From the ΔH values in the previous table and the values for the latent heats of vaporization, ΔH_{298} for the reaction = −26,900.

Assuming ΔH to be independent of temperature,

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{4.57}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$T_1 = 298, \qquad K_{p_1} = 1.6 \times 10^{13}$$

$$T_2 = 523(250^\circ C)., \qquad K_{p_2} = 5 \times 10^4$$

The conclusion is that this reaction has a tendency to go practically to completion at any temperature up to at least 250°C. Furthermore, a more rigorous calculation with accurate data would probably not alter the value of the constant enough to change the general conclusion. Thus a hundredfold change in the equilibrium constant in either direction would not make much difference.

The Nernst Approximation.—The method developed by Nernst for predicting equilibrium, based on the so-called "Nernst heat theorem" which later developed into the third law of thermodynamics, and utilizing the so-called "chemical constants," has been almost completely supplanted by the simpler and more logical treatment using the third law. The approximate equation given by Nernst

$$\log_{10} K_p = \frac{-\Delta H}{4.57\,T} + \Sigma n 1.75 \log_{10} T + \Sigma nC$$

where C is called by Nernst a "conventional chemical constant" to distinguish it from the chemical constants used in the more rigorous treatment, has been widely used in the past for predicting chemical equilibria; but it cannot be expected to give anything more than order-of-magnitude results, and its use should be superseded wherever possible by the more reliable methods illustrated above. Because it furnishes a very simple means of obtaining an approximate value of an equilibrium constant, its use may still be justified in a few instances. For this reason, one illustration of its use will be given.

Illustration 8.—Calculate the equilibrium constant for the methanol-synthesis reaction at 250°C. and 1 atm., using the Nernst approximation.

ΔH (assumed constant and equal to the value at 25°C.) = −22,000 (approximately)

C (chemical constant) for H_2 = 1.6, for CH_3OH = 3.5, and for CO = 3.5*

* Values of some conventional chemical constants are given in various physico-chemical tables. The following two empirical equations are also used for their calculation:

$$\Sigma n = -2, \qquad \Sigma nC = 3.5 - 3.5 - 2 \times 1.6 = -3.2$$

$$\log_{10} K_p = \frac{22,000}{4.57T} - 3.50 \log_{10} T - 3.2$$

$$T = 523, \qquad K_p = 3.2 \times 10^{-4}$$

From Illustration 4, the value based on the third law and on the latest experimental results is about 2×10^{-3}. The agreement is sufficiently close if one is interested only in determining whether or not a given reaction is at all feasible under a given set of conditions. As a matter of fact, this Nernst approximation value is much nearer the truth than many of the values that were based on the third law only a few years ago.

It must be admitted that the Nernst approximation does give surprisingly good results in many cases. The chief difficulty is that one cannot be certain how much reliance to put on the calculated result in any given instance. At the present time we should recommend its use only in those cases where the data to permit the use of the more rigorous methods are not available.[1]

EQUILIBRIUM CONVERSION

From the standpoint of the chemical engineer, the measurement or prediction of equilibrium constants is but a step toward the more important task of determining how far any reaction can proceed with a given set of conditions. Let us emphasize again that we shall be concerned with the *maximum possible* degree of completion of the reaction in question and not how far it will actually proceed in a given experiment. The maximum possible change is definitely determinable from thermodynamic considerations; but the actual change involves a consideration of catalysts, activation energies, and other factors classed as chemical kinetics, which are entirely outside the field of thermodynamics.

Homogeneous Gas Reaction.—We shall first consider any general homogeneous gas reaction taking place either in a continuous-flow system or in a static system, as represented by the equation,

$$aA + bB + \cdots = lL + mM + \cdots$$

$$C = 0.14 \frac{L}{T_B}$$

$$C = 1.7 \log_{10} p_c$$

where $L =$ latent heat of vaporization, g.-cal. per g.-mole.

$T_B =$ normal boiling, °K.

$p_c =$ critical pressure, atm.

[1] For further illustrations of the application of the Nernst approximation, the following references are suggested: PERRY, J. H., editor, "Chemical Engineers' Handbook," 2d ed., Section 5, McGraw-Hill Book Company, Inc., New York, 1941. TAYLOR, H. S., editor, "A Treatise on Physical Chemistry," Vol. 2, Chap. XVII, p. 1383, 1931. NERNST, W., "The New Heat Theorem" (translated from the second German edition by G. Barr, Methnen & Co., Ltd., London, 1926.

Let ζ = fraction of any given reactant such as A that is changed or converted when equilibrium is reached under a given set of conditions. Let N_A, N_B, N_L, N_M, etc., be the number of moles of the various reacting substances that are present in the initial mixture. In addition to these substances, let the initial gas contain N_I moles of gas that are inert as far as the particular reaction in question is concerned.

Let
$$r_B, r_L, r_M, \text{ etc. } = \frac{b}{a}, \frac{l}{a}, \frac{m}{a}, \text{ etc.}$$

When equilibrium has been reached, the following amounts of the various constituents will be present:

$$N_A(1 - \zeta) \text{ moles of } A = N_A^*$$
$$N_B - r_B N_A \zeta \text{ moles of } B = N_B^*$$
$$N_L + r_L N_A \zeta \text{ moles of } L = N_L^*$$
$$N_M + r_M N_A \zeta \text{ moles of } M = N_M^*$$
$$N_I \text{ moles of inerts}$$

Let ΣN = total moles of equilibrium mixture. The mole fraction of each constituent in the equilibrium mixture is the number of moles of that constituent divided by ΣN. Assuming an ideal gaseous solution and making use of Eqs. (XI.5) and (IV.254), one can write

$$\frac{(N_L^*)^l (N_M^*)^m \cdots}{(N_A^*)^a (N_B^*)^b \cdots} (\Sigma N)^{-\Sigma n} = \frac{K_f}{K_\gamma} p^{-\Sigma n} \tag{XI.27}$$

Each term in a parenthesis represents the number of moles of the particular gas present in the equilibrium mixture. For the special case of ideal gases, $K_\gamma = 1.00$. For any specified set of conditions, this equation can be solved for ζ, the fraction of A converted.

Illustration 9.—A gas mixture containing 60 per cent H_2, 20 per cent N_2, and 20 per cent inert gas is to be passed over a suitable catalyst to produce ammonia. If the pressure is 50 atm. and the final temperature is 400°C., what would be the maximum percentage of the hydrogen converted to NH_3 on one pass and what would be the per cent of NH_3 in the exit gases? Assume ideal gases.

The reaction is

$$\tfrac{3}{2}H_2 + \tfrac{1}{2}N_2 = NH_3$$
$$a = \tfrac{3}{2} \qquad b = \tfrac{1}{3} \qquad l = 1 \qquad r_B = \tfrac{1}{3} \qquad r_L = \tfrac{2}{3}$$
$$\Sigma n = 1 - \tfrac{1}{2} - \tfrac{3}{2} = -1$$
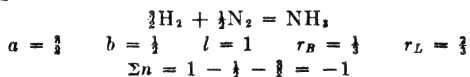
K_p° at 400°C. (from equation on page 494) = 0.0125. Take a basis of 100 moles of initial gas mixture and let ζ = fraction of hydrogen converted.

Moles in the equilibrium mixture:

$$H_2 = 60 (1 - \zeta)$$
$$N_2 = 20(1 - \zeta)$$
$$NH_3 = 40\zeta$$
$$\text{Inert} = 20$$

Total number of moles $\Sigma N = 100 - 40\zeta$

Substituting in Eq. (XI.27),

$$\frac{40\zeta}{[60(1 - \zeta)]^{\frac{3}{2}}[20(1 - \zeta)]^{\frac{1}{2}}} (100 - 40\zeta) = 50 \times 0.0125$$

This equation is best solved by trial. Let δ = difference between the two sides of the equation. Then $\delta = 0$ for the correct value of ζ. Trial values:

$$
\begin{array}{ll}
\zeta = 0.100, & \delta = 0.399 \\
\zeta = 0.200, & \delta = 0.075 \\
\zeta = 0.227, & \delta = -0.035 \\
\zeta = 0.218, & \delta = +0.005 \\
\zeta = 0.220, & \delta = -0.006 \\
\zeta = 0.219, & \delta = 0.000
\end{array}
$$

Therefore, 21.9 per cent of the hydrogen is converted to ammonia and the per cent of NH_3 in the exit gases is

$$\frac{(40\zeta)100}{100 - 40\zeta} = 9.6 \text{ per cent}$$

Illustration 10.—A gas mixture containing 25 per cent CO, 55 per cent H_2, and 20 per cent inert gas (all mole per cents) is to be used for methanol synthesis. If the gases issue from the catalyst chamber in chemical equilibrium with respect to the reaction

$$CO + 2H_2 = CH_3OH$$
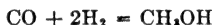
at a pressure of 300 atm. and temperature of 350°C., what per cent of the carbon monoxide will have been converted? Assume the equilibrium mixture is an ideal solution.

From (8) in Illustration 4, $K_f = 4.9 \times 10^{-5}$
From Fig. XI.3, $K_\gamma = 0.35$

Take a basis of 100 moles of initial gas mixture.

$$
\begin{aligned}
N_{CO}^* &= 25(1 - \zeta) \\
N_{H_2}^* &= 55 - 50\zeta \\
N_{CH_3OH}^* &= 25\zeta \\
\Sigma N &= 100 - 50\zeta
\end{aligned}
$$

Substituting in Eq. (XI.27),

$$\frac{\zeta(100 - 50\zeta)^2}{(1 - \zeta)(55 - 50\zeta)^2} = \frac{4.9 \times 10^{-5}(300)^2}{0.35}$$

$\zeta = 0.610$, or about 61 per cent of the CO would be converted. If ideal gases had been assumed, the value of ζ would have been 0.441.

Reaction in Gas and Liquid Phase.—The problem of estimating the equilibrium composition of a liquid solution resulting from a reaction in which both gas and liquid phases are present is a more difficult one. It can usually be solved only after a number of simplifying assumptions have been made. We shall first indicate the method of solution in a general form and then illustrate by a specific case.

Let us consider the reaction

$$aA + bB = cC$$
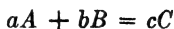
and assume that we wish to calculate the equilibrium concentration of C in the liquid phase at a given pressure and temperature. Assume that the standard state of each substance is chosen as the pure gas. The following equations can be written for any given temperature:

$$\frac{(a_C)^c}{(a_A)^a(a_B)^b} = K_a \tag{XI.28}$$

$$a_A'' = \phi_1''(p, y_A, y_B, y_C) \tag{XI.29}$$

$$a_B'' = \phi_2''(p, y_A, y_B, y_C) \tag{XI.30}$$

$$a_C'' = \phi_3''(p, y_A, y_B, y_C) \tag{XI.31}$$

These are equations for the activity in the gas phase. Similar equations could be written for the liquid phase, for example,

$$a_i' = \phi_i'(p, x_A, x_B, x_C)$$

Since we must have phase equilibrium,

$$\mu_i'' = \mu_i'$$

or, for a given standard state for any one substance,

$$a_i'' = a_i'$$

Thus we have the following equations:

$$\phi_1''(p, y_A, y_B, y_C) = \phi_1'(p, x_A, x_B, x_C) \tag{XI.32}$$

$$\phi_2''(p, y_A, y_B, y_C) = \phi_2'(p, x_A, x_B, x_C) \tag{XI.33}$$

$$\phi_3''(p, y_A, y_B, y_C) = \phi_3'(p, x_A, x_B, x_C) \tag{XI.34}$$

Obviously, the following equations are true:

$$x_A + x_B + x_C = 1 \tag{XI.35}$$

$$y_A + y_B + y_C = 1 \tag{XI.36}$$

Thus we have a minimum of nine equations and nine unknowns, and solution should be possible if we know K_a and the various functions denoted by ϕ. These would be quite complex for a ternary system even if we had the necessary data to represent them in a graphical form.

If one assumes an ideal solution in each phase, Eqs. (XI.29) to (XI.34) are greatly simplified and a numerical solution becomes practicable.

Thus Eq. (XI.29) reduces to the form

$$a_A = f_A = \phi(p)y_A \tag{XI.37}$$

and similarly for other activities.

$\phi(p)$ is the fugacity of pure A at the given pressure and temperature and is evaluated by methods previously discussed. Equation (XI.32) reduces to

$$y_A f_A'' = x_A f_A' \qquad (XI.38)$$

where f_A' and f_A'' are the fugacities of pure A at the given temperature and total pressure as a liquid and a vapor, respectively. In applying this equation one is faced with the necessity of evaluating the fugacity in an unstable state, as explained in Chap. IV.

The equations are still further simplified if one assumes ideal gases. On this assumption, Eq. (XI.29) becomes

$$a_A = f_A = y_A p \qquad (XI.39)$$

and Eq. (XI.32)

$$y_A p = x_A p_A \qquad (XI.40)$$

Utilizing Eqs. (XI.28), (XI.35), (XI.36), (XI.39), and (XI.40), one gets

$$K_a p^{-\Sigma n} = \frac{\left(x_C \dfrac{p_C}{p}\right)^c}{\left[1 - x_C \dfrac{p_C}{p} - \phi(x_C)\right]^a [\phi(x_C)]^b} \qquad (XI.41)$$

where

$$\phi(x_C) = \frac{p_B}{p}\left[\frac{p_A - p - x_C(p_A - p_C)}{p_A - p_B}\right]$$

This equation is readily solvable for x_C if the vapor pressures of the components are known at the temperature in question.

Illustration 11.—Estimate the maximum mole per cent of ethanol in the aqueous solution formed by reacting ethylene and liquid water at 254°C. in the presence of a suitable catalyst, the total pressure being maintained constant by connecting the reaction vessel to a source of ethylene at the constant pressure of 100 atm. Assume that the concentration of the catalyst is small enough so that it does not affect the activities of the reacting substances in solution. [*]

One must first calculate K_a for the reaction in question, and this involves a choice of standard states. Let us assume the standard state of each to be the pure gas at 1 atm. and that gases are ideal at this pressure. From the data on page 506 combined with the latent heat of vaporization of ethanol, 10,120 cal. per mole,[†] one readily gets, for the reaction,

$$C_2H_4 + H_2O(g) = C_2H_5OH(g)$$
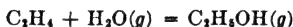
At 25°C.,
$$\Delta H = -11,000$$
$$\Delta S = -30.1$$
$$\Delta F = -11,000 + 298 \times 30.1 = -2,030$$

[*] This problem was taken from a paper by B. F. Dodge, *Trans. Am. Inst. Chem. Engrs.*, **34**, 529–567 (1938).

[†] ROSSINI, F. D., *Bur. Standards J. Research*, **13**, 189–202 (1934).

From this value and the specific-heat equations, we obtain, following Parks,[*]

$$\Delta F^\circ = -9{,}674 + 6.43T \ln T - 0.00665T^2 - 9.01T$$
$$T = 527, \qquad \Delta F^\circ = 4{,}980, \qquad K_a = 0.0085$$

Equation (XI.41) cannot be directly applied in this case because the temperature is above the critical temperatures of both ethylene and ethanol. Since it is so far above that of ethylene, we shall assume that the concentration of C_2H_4 in the liquid phase can be neglected, or that $x_A = 0$. This reduces Eq. (XI.41) to

$$K_a = \frac{x_C p_C}{[p - x_C p_C - (1 - x_C)p_B](1 - x_C)p_B} \tag{1}$$

p_C, the vapor pressure of ethanol at 527°K., can be obtained by only a slight extrapolation of the vapor-pressure curve beyond the critical point ($T = 516.3$, $p = 63.1$ atm.). Using the linear log p vs. $1/T$ relationship (see Chap. VI) for extrapolation,

$$p_C = 76 \text{ atm.}$$

Solving (1) by trial, $\qquad x_C = 0.195$

The experimental results of Gilliland and coworkers given on page 508 indicate a much smaller alcohol concentration. It may be that the assumption of an ideal solution for the alcohol introduces considerable error. This can be partly circumvented by choosing a different standard state for the ethanol, *viz.*, that of a dilute solution for which Henry's law can be assumed. Taking the standard state of water as the pure liquid, we have, from page 508,

$$K_a = 0.014 = \frac{a_C}{(a_A)(a_B)}$$

Again assuming ideal gases, no C_2H_4 in the liquid phase, and the liquid solution is ideal as far as the water is concerned,

$$a_C = m_C = \frac{55.5x_C}{1 - x_C}$$

(The relation between m and x follows at once from their definitions.)

$$a_A = y_A p$$
$$a_B = x_B = 1 - x_C$$
$$y_A = 1 - y_B - y_C$$
$$= 1 - \frac{x_B p_B}{p} - kx_C$$
$$= 1 - \frac{(1 - x_C)p_B}{p} - kx_C$$

k is the Henry law constant for the ethanol solution. Thus,

$$\frac{[55.5x_C/(1 - x_C)]}{[p - (1 - x_C)p_B - pkx_C](1 - x_C)} = 0.014$$

In the absence of data from which to evaluate k, we shall assume that the vapor pressure of the ethanol over the solution is given by the ideal-solution law, or that

$$k = \frac{p_C}{p}$$

[*] Parks, G. S., *Ind. Eng. Chem.*, **29**, 845–846 (1937).

Note that, although this is the same assumption made in the previous solution of the problem, it now, in effect, comes only into a correction term and does not have a major effect on the value of x_C.

Again solving for x_C by trial,

$$x_C = 0.015$$

This is in fair agreement with the experimental results previously quoted. Of course, both methods of calculation involve a number of approximations, and only order-of-magnitude results can be expected.

Isothermal vs. Adiabatic Reaction.—In making experimental measurements of equilibrium constants, reactions are always carried out under as nearly isothermal conditions as possible. When one uses equilibrium data to estimate possible conversions, one is apt to overlook the fact that all reactions are accompanied by heat effects. Heat must either be given out or absorbed if the isothermal condition is to be maintained. In experimenting on a small scale in the laboratory, dissipation or absorption of heat is a relatively simple matter, and it is not difficult to ensure isothermal conditions. On the other hand, when the reaction is conducted on a much larger scale, the addition or removal of heat becomes a serious problem and the reaction may, in many cases, be carried out under conditions more nearly adiabatic than isothermal. As far as the calculation of equilibrium conversion is concerned, it should make no difference what the thermal conditions are during the course of the reaction, provided that the final equilibrium state is established at some definite and known temperature.

In using equilibrium constants, one should have clearly in mind that the initial state of the reactants may be one quite different in temperature from the final state of the products. There are two limiting cases, (1) isothermal reaction and (2) adiabatic reaction; all actual cases would lie somewhere between these limits, but for purposes of calculation a close approach to either one or the other is generally assumed. In the case of gas reactions, especially when a contact catalyst is used, the problem of heat addition or removal is an especially difficult one. In large apparatus such reactions are apt to be carried out under conditions approaching relatively closely to the adiabatic case.

The importance of these considerations is illustrated in the following:

Illustration 12.—A gas consisting of two moles of hydrogen to one of carbon monoxide and no inerts enters a methanol catalyst chamber at 275°C. and 200 atm. pressure. The only reaction taking place may be assumed to be

$$CO + 2H_2 = CH_3OH$$
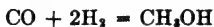
What is the maximum possible percentage conversion of CO to CH_3OH (1) if the reaction is adiabatic and (2) if it is isothermal?

1. *Adiabatic Case.*—Chemical equilibrium will be assumed for the gases leaving the catalyst, and this at once gives us a relationship between the degree of conversion

and the temperature. For the moment we shall indicate this equilibrium relationship by the general equation

$$\zeta = \phi_1(T) \tag{1}$$

where ζ = fraction of CO converted.

T = absolute temperature of gases leaving the catalyst.

The form of the function is known from considerations already discussed; but there are two unknowns, and, to obtain a solution, another equation between ζ and T is required.

This is furnished by the application of the first law as expressed by Eq. (IX.105), which for this particular case becomes:

$$\Sigma_P H - \Sigma_R H + \zeta \,\Delta H_{T_0} = 0 \tag{2}$$

This is readily put in the form

$$\zeta = \phi_2(T) \tag{3}$$

as follows:

Number of moles of reaction products = $(1 - \zeta)$ moles of CO
$+ 2(1 - \zeta)$ moles of H_2
$+ \zeta$ moles of CH_3OH

The heat capacities given in Illustration 1 will be used. This neglects the effect of pressure on C_p.

By taking the base temperature as the temperature at which the reactants enter, *viz.*, 548°K., we make

$$\Sigma_R H = 0$$

Then

$$\Sigma_P H = (1 - \zeta) \int_{548}^{T} (6.89 + 0.00038T)\, dT + 2(1 - \zeta) \int_{548}^{T} (6.65 + 0.00070T)\, dT$$
$$+ \zeta \int_{548}^{T} (2.0 + 0.03T)\, dT \tag{4}$$

Integrating and collecting terms,

$$\Sigma_P H = \zeta(0.0141T^2 - 18.19T + 5,726) + 0.00089T^2 + 20.19T - 11,322 \tag{5}$$

ΔH for the reaction at 275°C. is obtained from Eq. (IX.99) using the data of Illustrations 1 and 4. Thus,

$$\Delta H = -17,530 - 18.19T + 0.0141T^2$$
$$\Delta H_{548} = -23,250 \qquad \text{(per mole)}$$

or, for the reaction of ζ moles of CO, $\Delta H = -23,250\zeta$

Substituting in (2) and solving for ζ,

$$\zeta = \frac{-0.00089T^2 - 20.19T + 11,322}{0.0141T^2 - 18.19T - 17,524} \tag{6}$$

This is the development of (3). Now, (1) is developed as follows:

Assuming an ideal gaseous solution (not ideal gases), Eq. (XI.27) is applicable. Putting in the special conditions,

$$\frac{\zeta(3 - 2\zeta)^2}{4(1 - \zeta)^3} = \frac{p^2 K_f}{K_\gamma} \tag{7}$$

Both K_f and K_γ are functions of temperature, and so (7) is of the form of (1).

K_f is given by (8) in Illustration 4, and K_γ is given as a function of T by Fig. XI.3. The two simultaneous equations between ζ and T are readily solved by trial, and the following values are obtained:

$$T = 702°K. = 429°C.$$
$$\zeta = 0.140$$

2. *Isothermal Case.*

$$T = 548, \qquad K_f = 7.25 \times 10^{-4}, \qquad K_\gamma = 0.32$$

Solving (7),
$$\zeta = 0.84$$

The difference between the two cases is very striking. Even a small amount of cooling in the catalyst bed should bring about a substantial increase in the conversion. Another expedient that is used to increase the conversion is to carry out the reaction in more than one stage, with cooling between. This has been particularly developed in the contact process for sulphuric acid.

Autothermal Reactions.—The heat given out as a result of chemical reaction can be utilized to make the reaction autothermal, *i.e.*, thermally self-sustaining. For example, in the case of methanol synthesis, although outside heat must be added initially to bring the reactants up to the necessary temperature, once the reaction is started the products will be at a sufficiently higher temperature to permit heating up the reactants by use of a suitable heat exchanger.

FIG. XI.4.—Autothermal-reaction system.

Another interesting point in connection with autothermal reactions is worth brief discussion; this has to do with their thermal stability and its relation to their control. In the diagram of Fig. XI.4, consider an exothermic reaction taking place within the enclosure, which has been made self-sustaining by means of heat exchangers, and assume that the reacting system does not approach an equilibrium state. Let H_1 represent the total enthalpy of all the reactants entering the system and H_2 the same for the products leaving the system. If the heat-exchange system were perfect, the reaction products would be cooled back to the initial temperature; $H_1 - H_2$ would be the heat of reaction at the initial temperature of the reactants before they were preheated; and since $Q = H_1 - H_2$, the whole system must dissipate heat to the surroundings equal to the heat of reaction. Actually, of course, the products will leave with a higher enthalpy than this, and Q will be less than the heat of reaction; but the above relationship must hold in any case for a system in a steady state.

Now suppose that, owing to some change in conditions, the reaction rate increases and a higher degree of conversion tends to occur. Assuming no change in temperature of the final products leaving the system, $H_1 - H_2$ will increase, and therefore Q must increase to maintain the balance. This means that the temperatures in the system must increase; and this will cause a further increase in reaction rate, which in turn will call for a greater degree of reaction as long as equilibrium has not been reached. In other words, such a system is thermally unstable and may go entirely out of control. This can happen only if the reaction does not initially approach an equilibrium state. If it is substantially at equilibrium, any tendency for increase in the temperature is counteracted by the resulting smaller conversion. In other words, an autothermal reaction system at equilibrium is self-regulating.

A practical example of the working out of these ideas is seen in a methanol-synthesis converter where, in addition to the reaction

$$CO + 2H_2 = CH_3OH$$
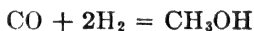
we have the possibility of other reactions, notably

$$CO + 3H_2 = CH_4 + H_2O$$
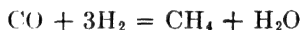
The first reaction approaches an equilibrium state; and since the equilibrium point changes very rapidly with temperature, the converter is relatively stable in temperature. The second reaction normally proceeds to only a slight extent; but if it should be favored by some change in conditions, it may get out of control and cause excessive temperatures in the converter because of the fact that the balancing effect of chemical equilibrium would not stop the reaction until a much higher temperature were reached.

Maximum Yield of Reaction Product.—The question sometimes arises as to the proportions in which the reactants should be mixed in order to obtain a maximum yield of a given product. For example, in the reaction

$$N_2 + O_2 = 2NO$$
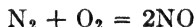
it may be desired to know what ratio of O_2 to N_2 will give a maximum yield of NO, in other words, a maximum concentration of NO in the product gases at equilibrium. (Note that this is not the same as the maximum percentage conversion.) Let us answer this for a more general case by considering the homogeneous reaction

$$aA + bB = lL + mM$$

Assume that the initial reactant mixture contains only A and B and that there are r_B moles of B per mole of A

On the basis of one mole of A initially, there will be in the equilibrium mixture

$$N_A \text{ moles of } A$$

$$r_B - \frac{b}{a}(1 - N_A) \text{ moles of } B$$

$$\frac{l}{a}(1 - N_A) \text{ moles of } L$$

$$\frac{m}{a}(1 - N_A) \text{ moles of } M$$

Let N = total number of moles.

x = mole fraction of M in the equilibrium mixture, and this is to be a maximum.

$$N_M = Nx = \frac{m}{a}(1 - N_A)$$

or $$N_A = 1 - \frac{a}{m}Nx$$

and $$N = \frac{1 + r_B}{1 + kx}$$

where $k = (a/m) + (b/m) - (l/m) - 1$.

With the aid of these equations, the mole fraction of each component in the equilibrium mixture can be expressed in terms of x. Assuming ideal gases and substituting in Eq. (XI.5) one gets

$$\frac{[(l/m)x]^l x^m}{\left(\dfrac{1+kx}{1+r_B} - \dfrac{a}{m}x\right)^a \left(\dfrac{r_B(1+kx)}{1+r_B} - \dfrac{b}{m}x\right)^b} = K \qquad \text{(XI.42)}$$

where $K = p^{-\Sigma n}K_p$.

To find the value of r_B that will make x a maximum, it is necessary only to apply the criterion

$$\frac{\partial x}{\partial r_B} = 0 \qquad \text{(XI.43)}$$

Differentiating Eq. (XI.42) and collecting terms,

$$\frac{\partial x}{\partial r_B} = \frac{K[(1+kx)/(1+r_B)^2](bX_1^a X_2^{b-1} - aX_1^{a-1}X_2^b)}{F} \qquad \text{(XI.44)}$$

F represents a complex algebraic expression that need not be developed in detail, and

$$X_1 = \frac{1+kx}{1+r_B} - \frac{a}{m}x$$

$$X_2 = \frac{r_B(1+kx)}{1+r_B} - \frac{b}{m}x$$

Applying Eq. (XI.43),

$$bX_1^a X_2^{b-1} = aX_1^{a-1} X_2^b$$

or
$$\frac{b}{a} = \frac{X_2}{X_1}$$

Substituting the values of X_2 and X_1 and clearing of fractions, one obtains

$$r_B = \frac{b}{a} \tag{XI.45}$$

Therefore, for maximum concentration of products in the equilibrium mixture, the reactants should be in the stoichiometric proportion. Although we have proved it only for the simple case of two reactants, it may be stated that the result is still true for any number of reactants.

It should be noted that this conclusion applies not only to the case of ideal gases but to any case where ideal solutions can be assumed.

SIMULTANEOUS REACTIONS

In all the previous discussion of chemical equilibrium, attention was focused on a single chemical reaction. In practice, one is more apt to be concerned with two or more reactions occurring simultaneously. This is particularly true in the field of organic chemistry in which, with a given set of reactants, many reactions may be possible. For example, considering the pair of reactants, carbon monoxide and hydrogen, an almost infinite variety of reactions can be written, of which the following are typical:

$$CO + H_2 = HCOH \tag{XI.46}$$
$$CO + 2H_2 = CH_3OH \tag{XI.47}$$
$$CO + 3H_2 = CH_4 + H_2O \tag{XI.48}$$
$$2CO + 5H_2 = C_2H_6 + 2H_2O \tag{XI.49}$$
$$3CO + 6H_2 = C_3H_7OH + 2H_2O \tag{XI.50}$$
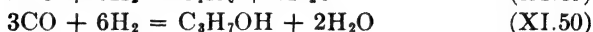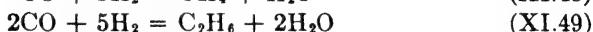
Obviously, a reaction such as Eq. (XI.50) could scarcely occur directly since that would require the simultaneous collision of nine molecules—an extremely improbable event. Undoubtedly, all these reactions after the first occur in a series of steps, but this is a question of mechanism upon which the laws of thermodynamics shed no light.

When one speaks of equilibrium in a reaction such as Eq. (XI.50), which is the result of several steps, he means that the concentrations of the four constituents satisfy a definite mass-action or equilibrium relationship even though various other constituents are also present. In general, one cannot calculate the expected maximum yield of any compound starting from CO and H_2 by assuming that the reaction that can be set down between this compound and the given reactants is the

only reaction that occurs. Strictly, one should consider simultaneous equilibria in all possible reactions between the substances involved. This is obviousiy impractical, but in many cases we can reduce the number of equations that need to be considered and arrive at a minimum for practical purposes.

For example, in considering the equilibrium in the methanol synthesis, we proceeded as if reaction (XI.47) were the only one that needed to be considered. This reaction undoubtedly proceeds by the two steps

$$CO + H_2 = HCOH \qquad (XI.51)$$
$$HCOH + H_2 = CH_3OH \qquad (XI.52)$$

and many side reactions are possible. Our calculations on the methanol equilibrium involved two implicit assumptions:

1. All side reactions proceed at a negligible rate in comparison with the rate of the reaction under consideration or of the steps in this reaction.

2. All intermediate products are so unstable that their concentrations at equilibrium are negligible in comparison with that of the main product.

These assumptions are implicit in all calculations on chemical equilibria; it is important to recognize this fact because in many cases they may not be good assumptions. In the case of the methanol equilibrium, they are valid assumptions because formaldehyde is very unstable under the conditions assumed and because a catalyst has been found that promotes the methanol reaction practically to the exclusion of all others. In the case of a reaction such as Eq. (XI.50) and many others involving a series of steps, it is probable that neither assumption is valid and we cannot expect to secure a high yield of product even though the value of the free-energy change for the reaction would indicate a very favorable equilibrium constant.

Since the free-energy change for a reaction is the sum of the free-energy changes for the individual steps, it follows that the equilibrium constant of the reaction is equal to the product of the constants for the step reactions. Thus considering Eq. (XI.47) as going by the steps (XI.51) and (XI.52), we can write

$$K_p \text{ (XI.47)} = K_p \text{ (XI.51)} \times K_p \text{ (XI.52)}$$

Suppose, purely for sake of illustration, that K_p (XI.47) at a reasonable reaction temperature is of the order of 10^{-3}. K_p (XI.51) and K_p (XI.52) could have an infinite variety of values and still satisfy the condition that their product should equal 10^{-3}. For example,

(a) $\qquad\qquad 10^{-3} = 10^{-10} \times 10^7$

(b) $\qquad\qquad 10^{-3} = 10^{-1} \times 10^{-2}$

(c) $\qquad\qquad 10^{-3} = 10^7 \times 10^{-10}$

(a) corresponds to a case in which the equilibrium concentration of the intermediate product, formaldehyde in this case, is very small, and the correct result would be obtained by considering only the over-all reaction as we have done in the case of the methanol synthesis reaction. In the case of (b) there would be considerable amounts of intermediate present, and one could not ignore it. In case (c) there would be mostly intermediate and a negligible amount of main product.

A reaction such as Eq. (XI.50) might be imagined to consist of six step reactions. From the considerations just discussed it is easy to see that a very favorable equilibrium constant for Eq. (XI.50) does not necessarily imply a good yield of propyl alcohol at equilibrium; in fact, the yield might be very small.

Quantitative Treatment.—To show how the equilibrium in a set of simultaneous reactions may be treated, we shall consider a simple case of two reactions with a common reactant and a common product and with a product of the first reaction becoming a reactant in the second, generalized as follows:

$$aA + bB = cC + dD \tag{XI.53}$$
$$cC + b'B = eE + d'D \tag{XI.54}$$

Assume that we start with an initial mixture of 1 mole of A and r_B moles of B.

Let N_A = number of moles of A reacting by Eq. (XI.53).

N_C = number of moles of C reacting by Eq. (XI.54).

At equilibrium with respect to both reactions there will be present

$$(1 - N_A) \text{ moles of } A$$

$$\left(r_B - \frac{b}{a} N_A - \frac{b'}{c} N_C \right) \text{ moles of } B$$

$$\left(\frac{c}{a} N_A - N_C \right) \text{ moles of } C$$

$$\left(\frac{d}{a} N_A + \frac{d'}{c} N_C \right) \text{ moles of } D$$

$$\frac{e}{c} N_C \text{ moles of } E$$

Total moles, $N = 1 + r_B + N_A \dfrac{c + d - b - a}{a} + N_C \dfrac{d' + e - b' -}{c}$

Assuming ideal gases, we have for equilibrium in Eq. (XI.53)

$$K_p p^{-\Sigma n} = \frac{\left(\dfrac{c}{a} N_A - N_C \right)^e \left(\dfrac{d}{a} N_A + \dfrac{d'}{C} N_C \right)^d}{(1 - N_A)^a \left(r_B - \dfrac{b}{a} N_A - \dfrac{b'}{c} N_C \right)^b} N^{-\Sigma n} \tag{XI.55}$$

and for equilibrium in Eq. (XI.54)

$$K_p p^{-\Sigma n} = \frac{\left(\dfrac{e}{c} N_C\right)^e \left(\dfrac{d}{a} N_A + \dfrac{d'}{c} N_C\right)^{d'}}{\left(\dfrac{c}{a} N_A - N_C\right)^c \left(r_B - \dfrac{b}{a} N_A - \dfrac{b'}{c} N_C\right)^{b'}} N^{-\Sigma n} \quad (XI.56)$$

These two equations must be satisfied simultaneously.

Illustration 13.—What is the maximum per cent of methanol to be expected in the gases issuing from a reaction chamber if a mixture of two moles of H_2 to one of CO were passed over a catalyst that permitted the attainment of equilibrium with respect to the two reactions

$$CO + 2H_2 = CH_3OH(g) \tag{1}$$
$$CH_3OH(g) + H_2 = CH_4 + H_2O(g) \tag{2}$$
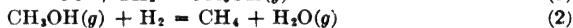
at 600°K. and 100 atm.?

For the standard free-energy change of (1) use can be made of the equation in Illustration 4. This gives, for 600°K.,

$$K_p = 8.3 \times 10^{-5}$$

To obtain an equilibrium constant for (2) we shall utilize the equations of Eastman[1] for the free energy of formation of CO and H_2O as a function of temperature and the equation of Thomas, Egloff, and Morrell[2] for CH_4, along with the equation for the free-energy change of (1), and obtain

$$\Delta F^\circ_{600} = -29,120, \qquad K_p \text{ at } 600 = 7.86 \times 10^{10}$$

Without setting up the mass-action equations it is evident by inspection of the constants that the percentage of methanol in the converted gases will be negligible. This emphasizes the interesting fact that the success of the methanol synthesis depends on suppression of reaction (2). The catalysts used are so specific that this reaction occurs to a negligible extent.

Illustration 14.—In a proposed process for producing hydrogen, methane and steam are to be passed over a catalyst at atmospheric pressure. It is desired to know the per cent of methane decomposed and the composition of the dry off-gas if five moles of steam to one of CH_4 is used and if it can be assumed that the gases leaving the reactor are in equilibrium at 600°C.

Many reactions are possible in such a system, for example,

$$CH_4 + H_2O = CO + 3H_2 \tag{1}$$
$$CH_4 + 2H_2O = CO_2 + 4H_2 \tag{2}$$
$$CH_4 = C + 2H_2 \tag{3}$$
$$CO + H_2O = CO_2 + H_2 \tag{4}$$
$$CO_2 + C = 2CO \tag{5}$$
$$CO_2 = C + O_2 \tag{6}$$
$$2CO = 2C + O_2 \tag{7}$$
$$H_2O = H_2 + \tfrac{1}{2}O_2 \tag{8}$$
$$H_2O + C = H_2 + CO \tag{9}$$
$$2CH_4 = C_2H_6 + H_2 \tag{10}$$
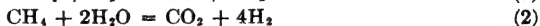
[1] EASTMAN, E. D., *Bur. Mines Inf. Circ.* 6125 (1929).

[2] THOMAS, C. L., G. EGLOFF, and J. C. MORRELL, *Ind. Eng. Chem.*, **29**, 1260-1267 (1937).

$$C_2H_6 = C_2H_4 + H_2 \qquad (11)$$
$$\text{etc.}$$

(All substances are assumed to be in the gaseous state except carbon.)

This looks like a very complex situation but a little analysis will enable one to make a great simplification. In the first place, these are not all independent reactions, and we can eliminate some on this basis. Thus, $(2) = (1) + (4)$, $(7) = (6) - (5)$, $(9) = (8) - \frac{1}{2}(7)$, and $(1) = (3) + (9)$. As a result of these relations we can eliminate four equations, for example, (2), (3), (7), and (9). There is, of course, nothing special about the elimination of these particular equations. Any four of the nine could be chosen for elimination. (6) and (8) can be neglected since a consideration of the free energies of these two reactions would show that they could proceed only to a very slight extent at this temperature. Similarly, it can be shown that (10) would not proceed to any appreciable extent, and this automatically eliminates (11). We shall arbitrarily eliminate reaction (5) from consideration and justify this step later. This leaves only reactions (1) and (4) to be considered. The standard free-energy equations for these two reactions will be based on the following data:

Heats of combustion at 25°C. to form liquid water:

$$H_2, \ \Delta H = -68{,}313$$
$$CO, \ \Delta H = -67{,}623$$
$$C, \ \Delta H = -94{,}240$$
$$CH_4, \ \Delta H = -212{,}790$$
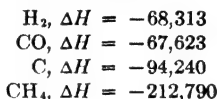
Entropies at 25°C. and ideal-gas state:

$$H_2, \ S = 31.23$$
$$CO, \ S = 47.32$$
$$CO_2, \ S = 51.10$$
$$H_2O, \ S = 45.17$$
$$CH_4, \ S = 44.46$$
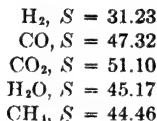
Specific heats as functions of temperature at 1 atm.:

$$H_2, \ C_p = 6.947 - 0.200 \times 10^{-3}T + 4.808 \times 10^{-7}T^2$$
$$CO, \ C_p = 6.342 + 1.836 \times 10^{-3}T - 2.801 \times 10^{-7}T^2$$
$$H_2O, \ C_p = 7.187 + 2.373 \times 10^{-3}T + 2.084 \times 10^{-7}T^2$$
$$CO_2, \ C_p = 6.396 + 10.193 \times 10^{-3}T - 35.193 \times 10^{-7}T^2$$
$$CH_4, \ C_p = 3.38 + 0.017903T - 4.188 \times 10^{-6}T^2$$
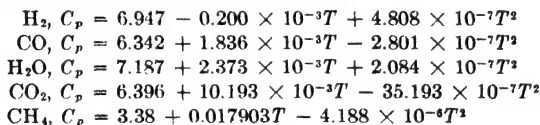
Units in all cases are gram-calories, gram-moles, and degrees Kelvin.

From these data the following equations are obtained:

For reaction (1)

$$\Delta F^\circ = 45{,}118 - 16.616T \ln T + 9.52 \times 10^{-3}T^2 - 8.57 \times 10^{-7}T^3 + 54.40T$$

For reaction (4)

$$\Delta F^\circ = -9{,}985 + 0.186T \ln T - 2.892 \times 10^{-3}T^2 + 4.945 \times 10^{-7}T^3 + 10.51T$$

At $T = 873$ $(t = 600°C.)$, $\quad \Delta F_1^\circ = 1{,}060, \qquad K_{p_1} = 0.54$
$$\Delta F_4^\circ = -1{,}585, \qquad K_{p_4} = 2.49$$

In Eqs. (XI.55) and (XI.56),

$$a = b = c = b' = e = d' = 1$$
$$d = 3, \qquad N = 5$$
$$\Sigma n \text{ for Eq. (XI.55)} = 2$$
$$\text{for Eq. (XI.56)} = 0$$
$$N = 6 + 2N_4$$

Substituting in Eqs. (XI.55) and (XI.56),

$$\frac{(N_A - N_C)(3N_A + N_C)^3}{(1 - N_A)(5 - N_A - N_C)(6 + 2N_A)^2} = 0.54 \tag{12}$$

$$\frac{N_C(3N_A + N_C)}{(N_A - N_C)(5 - N_A - N_C)} = 2.49 \tag{13}$$

Solving (12) and (13) by trial,

$$N_A = 0.911, \qquad N_C = 0.653$$

Therefore, 91 per cent of the methane would be decomposed.

$$\text{Total moles of dry off-gas} = 6 + 2N_A - \left(r_B - \frac{b}{a}N_A - \frac{b'}{c}N_C\right) = 4.386$$

$$\text{Moles CH}_4 = 1 - N_A = 0.089$$

$$\text{Moles CO} = \frac{c}{a}N_A - N_C = 0.258$$

$$\text{Moles H}_2 = \frac{d}{a}N_A + \frac{d'}{c}N_C = 3.386$$

$$\text{Moles CO}_2 = \frac{e}{c}N_C = 0.653$$

Composition of dry gas:

> 77.2 per cent H_2
> 14.9 per cent CO_2
> 5.9 per cent CO
> 2.0 per cent CH_4

Let us return to a consideration of reaction (5) and see if carbon deposition is possible.

For this reaction,

$$\frac{K_p}{p} = \frac{x_{CO}^2}{x_{CO_2}}$$

The value of x_{CO}^2/x_{CO_2} must be equal to or greater than K_p/p in order to have carbon deposition. From the free-energy equation for this reaction given by Lewis and Randall,[1] K_p at 600°C. = 0.083.

$$\frac{x_{CO}^2}{x_{CO_2}} \text{ in the equilibrium mixture} = 0.0234$$

Thus carbon deposition is not possible at equilibrium in this system and our elimination of (5) is justified.

A paper by the author[2] may be consulted for some further details on the application of thermodynamics to chemical reactions and particularly for a large number of references to equilibrium data on specific reactions.[3]

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[1] Lewis, G. N., and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.

[2] Dodge, B. F., *Trans. Am. Inst. Chem. Eng.*, **34**, 529–568 (1938).

[3] The problem just solved was also taken from the paper in reference 2.

CHAPTER XII

VAPORIZATION AND CONDENSATION EQUILIBRIA

The group of unit operations that is sometimes known as the "vaporization processes" and that includes such important and widely used operations as distillation, rectification, condensation, evaporation, drying, humidification, and absorption can be advantageously treated from the viewpoint of thermodynamics. The classification of the various processes under the heads given above is useful but far from precise, and there is bound to be a certain amount of confusion with respect to terminology. However, these vaporization processes are all related by virtue of the fact that they involve a material transfer between phases in contact—generally between gas and liquid phases though solid phases would be involved in adsorption and sublimation—and the rates of transfer are believed to be governed to a greater or lesser extent (less in evaporation, for example, than in absorption) by diffusion. When the transfer occurs from a liquid to a vapor phase, the process is frequently referred to as "vaporization" and the reverse process is called "condensation" or "liquefaction." From elementary kinetic theory we know that both processes are occurring simultaneously whenever liquid and vapor phases are in contact and what is observed is the net result of the rates of the two opposing processes. When the rates are equal and no net interchange takes place, the system is said to be "at equilibrium." In this state, a slight shift in one of the state variables—pressure, temperature, or concentration—will cause the process to proceed in either direction, and a significant change in one of these variables will cause one or the other of these fundamental processes to predominate so that the net result is clearly recognizable as a vaporization or a condensation.

We shall therefore regard vaporization and condensation as the fundamental processes involved in all the unit operations mentioned above and for that reason have chosen the title of the chapter to include them. In the development of the subject we shall lean heavily toward the operations of distillation and rectification in which a liquid solution is separated into two or more fractions that may or may not be substantially pure components, but we shall also treat the case of one or more condensable components being liquefied from a mixture including noncondensable gases.

From a broad general standpoint, all processes involving transfer of material between phases, whether gaseous, liquid, or solid, are essen-

tially similar, and we should be able to develop relationships sufficiently general to treat any one of them when the special conditions are imposed. Several attempts along this line have been made,[1] but in the present state of development of this general method we believe it is less confusing to adhere to the common practice of dividing the subject into more or less arbitrary subdivisions and treating each individually.

The application of thermodynamics to these processes is mainly concerned with:

1. The study of the various types of phase equilibria involved in order to determine the limiting possible conditions of separation.

2. Energy requirements for the process.

3. Efficiencies and the distribution of the "losses."

4. The number of units (transfer units, plates, etc.) required for a given separation.

Mass transfer of a given component between phases occurs only when differences in chemical potential of the component exist. When all the potentials are equalized, equilibrium between the phases exists. The distance from equilibrium is the driving force causing change, and the rate of the transfer will therefore depend on the distance from equilibrium. The conditions of pressure, temperature, and composition of the phases at equilibrium are fundamental to any discussion of the vaporization processes. The treatment of the various types of equilibria that are encountered, particularly in distillation, forms the subject matter of this chapter. Distillation processes will be considered in the next chapter.

Phase Rule.—The phase rule is a useful and indispensable guide through the complex mass of data that has now accumulated on many systems. It is so simple and now so taken for granted that it is difficult to realize to what extent our whole structure of phase-equilibrium relationships rests on it as a solid foundation. Although it was discussed in Chap. VI in connection with the study of thermodynamic properties, it is desirable to consider it again at this point, even at the risk of some duplication.

The rule (see Chap. IV for derivation) is stated

$$D = N - Z + 2 \qquad (\text{IV.122})$$

where D = number of degrees of freedom or number of independent variables.

N = number of components.

Z = number of phases.

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[1] See, for example, papers by RANDALL, M., and B. LONGTIN, *Ind. Eng. Chem.*, **30**, 1063–1067, 1188–1192, 1311–1315 (1938).

If we have a system of two components—ethyl alcohol and water, for example—and two phases—one liquid and one vapor—there are two degrees of freedom. This means that we can fix any two of the variables of the system more or less arbitrarily (within certain limits, of course—if the temperature were set above the boiling point of the less volatile component at the pressure chosen, no liquid phase would be possible) and when we have done so the state of the system is definitely determined. Thus, in the case of alcohol and water, if we set the pressure at 1 atm., the temperature can arbitrarily be set at any point between the limits of 100 and 78.5°C. When both are fixed, then the compositions of the two phases are also fixed. If we should attempt to alter the composition of either phase, still keeping the pressure and temperature constant, one of the phases must disappear. If a binary system forms two liquid phases in addition to the one vapor phase, then the system is univariant (one degree of freedom) and its state is determined by its temperature alone or its pressure or the composition of one of the phases. If a fourth phase —a solid, for example—were also present, the system would be invariant, *i.e.*, this particular state of affairs could exist at only one point and no variation at all in conditions is possible without causing the disappearance of a phase.

The variables of state most important in distillation are pressure, temperature, composition of liquid phases, and composition of vapor phase. For a binary, two-phase system, the one with which we shall be most concerned, the following kinds of phase-equilibrium, or boundary, curves involving these four variables are possible according to the phase rule:

(1) p vs. t at constant x
(2) p vs. t at constant y
(3) p vs. x at constant t
(4) p vs. x at constant y
(5) p vs. y at constant t
(6) p vs. y at constant x
(7) t vs. x at constant p
(8) t vs. y at constant p
(9) t vs. x at constant y
(10) t vs. y at constant x
(11) y vs. x at constant p
(12) y vs. x at constant t

The relationships numbered (4), (6), (9), and (10) are of little importance and will not be referred to again. All the other eight relationships will be illustrated later in the chapter. Relationships at constant pressure are the most important from an industrial standpoint since most distillation processes operate under this condition. On the other hand,

it is perhaps somewhat more convenient to maintain constant temperature in the laboratory, and hence most of the published data on phase equilibrium are for isothermal conditions. Some treatises on phase equilibrium[1] use volume as one of the coordinates in the graphical representation of phase equilibria. The use of volume has some advantages in considering systems at elevated pressures, especially in the critical region, but no use will be made of it in this text.

A *pt* boundary curve is generally called a "vapor-pressure curve," though this term is usually restricted to the liquid branch or the *pt* curve at constant *x*. *px* and *tx* curves are referred to as "liquid lines" or "bubble-point lines" since they relate the pressure (or the temperature) to the composition of the total system when the liquid is in equilibrium with a negligible amount (single bubble) of vapor. A *tx* curve is also called a "boiling-point line." Similarly, *py* or *ty* curves are called "vapor lines" or "dew-point lines" since they relate the pressure (or temperature) to the composition of the total system when the vapor is in equilibrium with a negligible amount of liquid (dew). These boundary curves also outline the fields in which certain phases or mixtures of phases (heterogeneous system) are stable.

In addition to the boundary curves limiting the fields of stability of the phases, which appear on phase-equilibrium diagrams, one also needs lines that connect the compositions of the two phases that coexist at equilibrium. Such lines are called "tie lines." In the case of pressure-composition or temperature-composition diagrams, the tie lines are always horizontal (since the coexisting phases must be at the same pressure or temperature) and hence need not be shown; but on some other diagrams such as enthalpy-concentration, volume-concentration, or ternary composition diagrams it is convenient to show tie lines.

Note that *p* in the discussion above always refers to the total pressure, which is the only kind of pressure that can be experimentally observed and controlled. In certain instances it is convenient to deal with a partial pressure, but it should be recognized that this is purely a mathematically defined quantity and not a variable of state.

Miscibility.—Three general cases of miscibility arise in distillation practice. The first and simplest case is that in which the two components in question are immiscible in the liquid phase. There are probably no pairs of actual liquids that are entirely immiscible; but there are many pairs, particularly many organic liquids with water, that are so slightly miscible as to be regarded as immiscible for all practical purposes. Immiscibility is therefore a limiting case that actual systems approach more or less closely but never quite reach. Probably a system such as

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[1] For example, KUENEN, J. P., "Theorie der Verdampfung und Verflüssigung von Gemischen, und der fraktionierten Destillation," J. A. Barth, Leipzig, 1906.

mercury-water comes as near to this limiting case as any, and certainly for all practical purposes these two liquids are immiscible. Although we could treat a multicomponent system in which each component formed a pure liquid phase just as easily as we could a binary system, there are few cases where more than two liquid phases coexist and none of any practical importance.

The commonest and most important case is that in which the liquid components are completely miscible over the whole range of composition and hence only one liquid phase can exist. The great majority of organic liquid mixtures fall into this category.

Intermediate between these two limiting cases is that of partial miscibility in which there is only one liquid phase over a portion of the concentration range and two over the remainder.

The dividing line between these classes is by no means a sharp one. Systems that are substantially immiscible at one temperature become partially miscible as the temperature is increased, and many partially miscible systems become wholly miscible above (and in some cases below) a certain critical temperature.

The degree of miscibility is obviously related to the fields of force surrounding the molecules. Where two substances have similar fields of force, they would be expected to mix in all proportions. Where they are widely different, as in the case of a polar liquid like water and a nonpolar one like benzene, we get almost complete immiscibility. As the organic liquid tends toward the polar type, we find a higher degree of miscibility with water; finally, with a compound such as ethyl alcohol, complete miscibility obtains. Liquids that are very similar, such as benzene and toluene or methyl alcohol and ethyl alcohol, would be expected to mix with a minimum of change of properties of the solution from that expected on the basis of strict additivity (ideal solutions).

Most of the cases of partial miscibility occur when one of the pair of liquids is water or some other inorganic liquid, but there are a number of cases in which organic liquid pairs are only partially miscible over certain ranges. For example, the following pairs exhibit partial miscibility: carbon disulphide–methyl alcohol; hexane–ethyl alcohol; amylene-aniline; acetic acid–benzene; methyl alcohol–acetone. As the temperature is changed, one would expect to reach a point where almost any pair of liquids would become only partially miscible, but usually either a solid phase appears or a critical point is reached before this temperature is attained.

Immiscible Liquids.—The equilibrium relationships even in multicomponent systems are relatively simple since there is only one degree of freedom and all the liquid phases contain only the pure components. Thus the *pt* relation is a single curve independent of the relative amounts

of the various components that are present.   The vapor pressure of any mixture is merely the sum of the vapor pressures of the individual components.   The boiling point is independent of composition and is the temperature at which the sum of the vapor pressures of the pure components is equal to the total pressure.   It is obviously lower than that
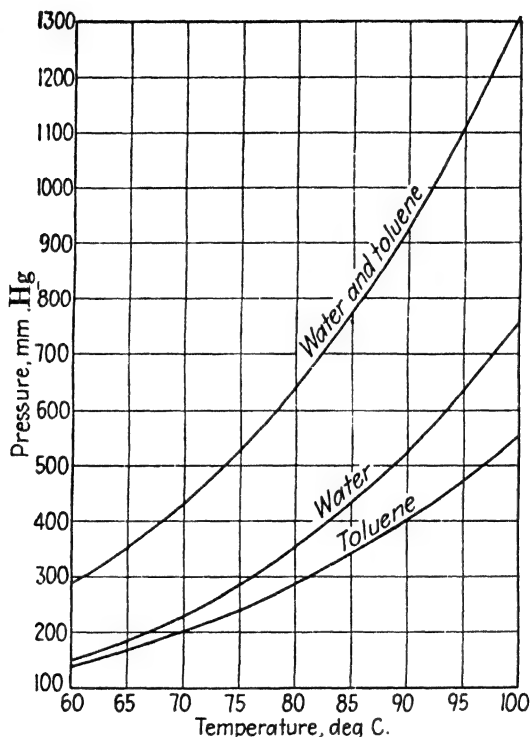
FIG. XII.1.—Vapor pressures in the toluene-water system.

of any component.   The composition of the equilibrium vapor is readily calculated from the vapor pressures if the ideal-gas law can be assumed.

Illustration 1.—Calculate the normal boiling point of toluene-water mixtures and the composition of the equilibrium vapor, assuming complete immiscibility.   The vapor pressures of the two components are as follows:

t, °C..................................	60	70	80	90	100
Vapor pressure of water, mm. Hg........	149	234	355	526	760
Vapor pressure of toluene, mm. Hg.....	139	206	287	404	557

Plotting the sum of the two pressures against the temperature, the intersection with the 760-mm. pressure line is found to be at 84.5°C. (Fig. XII.1). From the vapor-pressure curves of the two components the vapor pressures at this temperature are

Water, 427 mm. Hg.

Toluene, 333 mm. Hg.

Assuming the vapor to be a mixture of ideal gases, the mole fraction of toluene in the vapor is

$$\frac{p_T}{760} = \frac{333}{760} = 0.438$$

In dealing with binary systems of immiscible liquids one is interested not only in the three-phase system but in the possible two-phase systems as well. From the phase rule it is clear that there is only one particular vapor in equilibrium with both liquid phases; but a single liquid phase can be in equilibrium with a whole series of vapors at different temperatures, assuming the total pressure to be fixed. The complete diagram for this case is shown in Fig. XII.2. *DE* is the boiling-point line for the mixture of two liquid phases; *BC* the dew-point line for vapors richer in *B* than the vapor at *C*, which is the single vapor for three-phase equilibrium; *CA* is the dew-point line for vapors richer in *A* than the vapor at *C*. Horizontal lines such as *FG* and *HI* are tie lines connecting coexisting phases. Clearly, any vapor whose composition is to the left of *C* will be in equilibrium with pure liquid *B*, and any vapor whose composition is to the right of *C* will be in equilibrium with pure liquid *A*.[*]
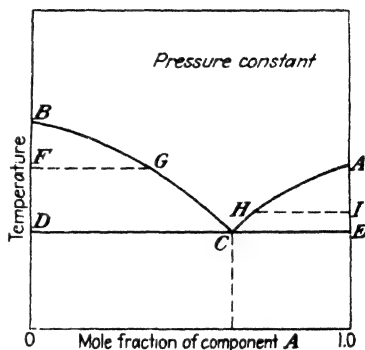
Fig. XII.2.—Temperature-composition diagram for two immiscible liquids.

COMPLETELY MISCIBLE LIQUIDS

The commonest case in distillation and related processes is the separation of mixtures (more strictly solutions) of substances that are miscible in all proportions. The great majority of all organic liquids form solutions of this type. The treatment to follow will be limited to the case of binary solutions except where otherwise explicitly indicated.

Ideal Solutions.—This is a limiting case for which the liquid-vapor equilibrium relationships are particularly simple and hence a good case

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[*] Those who are familiar with the types of equilibrium diagrams encountered in dealing with alloys will recognize this as the same type that applies to the common case of two solids that crystallize separately to form a eutectic.

with which to start our discussion. For the definition of an ideal solution, reference should be made to Chap. IV. Pairs of liquids that are similar in chemical structure, such as some types of isomers and adjacent members of homologous series, would be expected to form nearly ideal solutions. The following pairs of liquids are typical: benzene-toluene; hexane-heptane; n-octane–2,2,4-trimethyl pentane; ethyl alcohol–methyl alcohol; ethyl acetate–ethyl propionate. Solutions in which the components differ only in isotopic composition, for example, ordinary water, H_2O, and heavy water, D_2O, would be expected to follow the ideal-solution laws very exactly.

There are three criteria that are useful for an experimental test of an ideal solution, *viz.*,

1. Negligible volume change on mixing.
2. Negligible temperature change on mixing (no heat of mixing).
3. Total vapor pressure is a linear function of composition.

Criterion (1) follows from the definition of an ideal solution; (2) and (3) follow logically from (1), as was shown in Chap. IV, provided that the vapor can be assumed an ideal gas. The following shows some typical data on volume and temperature changes for mixing at room temperature of equimolal proportions of two liquids:[1]

Mixture	Per cent change in volume on mixing	Temperature change, °C.
n-Octane / n-Hexane	-0.053	$+0.06$
Benzene / Toluene	$+0.161$	-0.45
Ethyl alcohol / Methyl alcohol	$+0.004$	-0.10
Water / Methyl alcohol	-2.98	$+7.85$
Benzene / Ethyl alcohol	0.00	-4.2

The first three pairs would be expected to form ideal solutions because of their chemical similarity, and the two criteria confirm this. Likewise, the last two pairs would not be expected to be ideal, and this is confirmed by the criteria except in the case of benzene–ethyl alcohol where no volume change on mixing occurs. This illustrates the fact that negligible volume or temperature change for one particular mixture is not a safe criterion of an ideal solution. The reason for this is shown in Fig. XII.3.

[1] YOUNG, S., "Distillation Principles and Processes," The Macmillan Company, New York, 1922.

The broken line represents the volume of an ideal mixture of components *A* and *B* as a function of the composition, and the solid line depicts a case that may exist for a nonideal solution. It is clear that, when the components are mixed in the proportion represented by point *P*, no volume change will occur but for every other proportion of the components there will be a volume change. The conclusion is that criteria (1) and (2) should be applied at more than one composition of the solution. Undoubtedly criterion (3) is the most reliable but not so easy to apply as the other two. The first three of the above pairs of liquids exhibit a nearly linear vapor-pressure curve (*p* vs. *x*), whereas the other two do not; from this fact it is safe to conclude that only the first three form substantially ideal solutions.

It is important to have a good test for an ideal solution because accurate vapor compositions are very difficult to determine and can be very easily calculated provided that one can be sure that the solution is ideal.[1] In the cases where the relative volatility (ratio of the vapor pressures of the two pure components) is not far from 1.00, small errors in experimentally

FIG. XII.3.—Volume change accompanying the mixing of two completely miscible liquids.

determined vapor compositions may have a large effect on distillation calculations, and hence calculated vapor compositions are desirable.

The most important equations applying to the case of ideal solutions with the vapor phase an ideal gas are as follows (from Chap. IV):

$$p = p_A x + p_B(1 - x) \qquad (IV.177)$$

$$\frac{y}{1 - y} = \frac{p_A}{p_B} \frac{x}{1 - x} \qquad (IV.178)$$

$$yp = \bar{p}_A = p_A x \qquad (IV.180)$$

$$(1 - y)p = \bar{p}_B = p_B(1 - x) \qquad (IV.181)$$

Equation (IV.178) may also be put in the forms

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \qquad (XII.1)[2]$$

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[1] It should perhaps be emphasized that the ideal solution is, like the ideal gas, only a limiting case to which actual solutions approach more or less closely. In a number of cases the approach is close enough for practical purposes. One must also bear in mind that the usual equations assume that the vapor is an ideal gas, and saturated vapors even at 1 atm. may deviate several per cent from the ideal gas laws.

[2] This equation and also Eq. (IV.178) involve ratios of the masses of a given com-

and
$$x = \frac{y}{\alpha - (\alpha - 1)y} \qquad (XII.2)$$

and Eq (IV.177) in the form

$$x = \frac{p - p_B}{p_A - p_B} \qquad (XII.3)$$

Eliminating x from Eq. (IV.178) by Eq. (XII.3), we l ave

$$y = \frac{p_A(p - p_B)}{p(p_A - p_b)} \qquad (XII.4)$$

and
$$p = \frac{p_A p_B}{p_A - (p_A - p_B)y} \qquad (XII.5)$$

These equations are represented graphically in Figs. XII.4 and XII.5 for the case of a constant temperature.   In Fig. XII.4, the liquid line, or
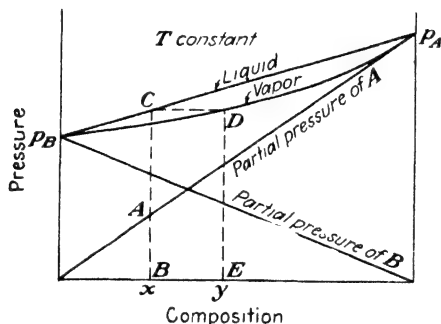
Fig. XII.4.—Pressure-composition diagram for the case of ideal liquid solution and ideal gas.

bubble-point line, is the graph of Eq. (IV.177).   The vapor line, or dew-point line, is the graph of Eq. (XII.4).   The partial-pressure lines are the graphs of Eqs. (IV.180) and (IV.181), respectively.   Figure XII.5 shows the graph of Eq. (XII.1).

All the lines on Fig. XII.4 are very simply obtained from a knowledge only of p_A and p_B, the vapor pressures of the two pure components, by using either the equations just given or a purely graphical construction that is self-explanatory for the three straight lines.   Since, by Eq. (IV.180),

$$y = \frac{p_A x}{p} = \frac{\bar{p}_A}{p}$$

ponent, and hence the concentration can be expressed either in mole fractions or in weight fractions. α is the relative volatility, and it may sometimes be taken as a constant even though the solution is not ideal and the vapor deviates from the ideal gas law.

it is evident that points on the vapor curve are obtained by dividing the intercept on the ordinate at x, formed by the line representing the partial pressure of A, by the corresponding intercept formed by the total pressure or liquid line, or $y = \overline{AB}/\overline{CB}$. This locates the vapor point D, which must be at the same pressure as the point C on the liquid line. These two points, corresponding to compositions of liquid (x_B) and of vapor (y_E) at the same pressure and temperature, must represent the composition of liquid and vapor phases at equilibrium. By the same token, any horizontal (constant-pressure) line between the limits of p_A and p_B will intersect the liquid and vapor lines at points representing compositions of the coexisting phases in equilibrium.

In cases where only a few calculations are to be made, it is generally
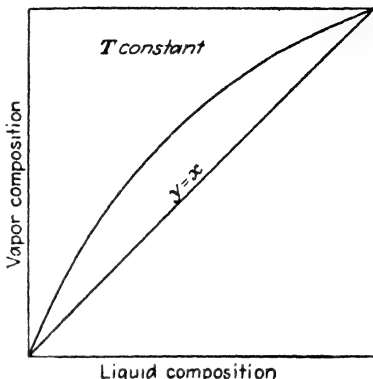
Fig. XII.5.—Vapor-composition—liquid-composition (yx) diagram for ideal solution.

simpler to use the equations directly rather than to use them to first construct a px diagram. The following illustrates one type of calculation that can be made.

Illustration 2.—An equimolal solution of benzene and toluene (to be assumed ideal) is totally evaporated at a constant temperature of 90°C. What are the pressures at the beginning and the end of the vaporization process? Vapor pressures of benzene and toluene are 1,008 mm. and 404 mm., respectively, at 90°C.

By Eq. (IV.177), $p_1 = 0.500 \times 1,008 + 0.500 \times 404 = 706$ mm.

At end of vaporization, $y = 0.500$ and p_2 is given by Eq. (XII.5).

$$p_2 = \frac{1,008 \times 404}{1,008 - (1,008 - 404)0.500} = 576 \text{ mm.}$$

Actual distillations are carried out at constant pressure rather than at constant temperature, and hence equilibrium relationships for constant pressure are more useful. There are no simple equations like those just given, relating temperature and composition at constant pressure, but the data or the corresponding graphs are readily obtained from Eqs. (XII.1) and (XII.3) by applying them at a series of temperatures between the boiling points of the two pure components, as shown in the following example.

Illustration 3.—Calculate data from which to construct tx and yx diagrams for the system benzene-toluene at a pressure of 1 atm., given the following vapor-pressure data for the pure components:

t, °C.............................	70	80	90	100	110	120
Vapor pressure of benzene, mm. Hg..	540	756	1,008	1,338	1,740	2,215
Vapor pressure of toluene, mm. Hg...	206	287	404	557	741	990

Assume ideal solution and ideal gas.

By plotting these data and locating the intersections of the vapor-pressure curves with the $p = 760$ abscissa, the boiling points of the pure components are determined as 80.2°C. and 110 5°C., respectively. A series of temperatures is then arbitrarily chosen between these limits, the corresponding vapor pressures read from the graphs, and x and y calculated from Eqs. (XII.3) and (XII.1), respectively. The results are tabulated below:

t, °C.	p_B, mm.	p_T, mm.	$\dfrac{p_B}{p_T}$	x	y	y (from average α)
80.2	760	288	2.64	1.00	1 00	
82.0	815	307	2.65	0.892	0.957	0 953
85.0	877	340	2.58	0.782	0 903	0 900
90.0	1,008	404	2 50	0.590	0.782	0.782
95.0	1,150	475	2 42	0.422	0.640	0 645
100.0	1,338	557	2.40	0.260	0.457	0 466
105.0	1,530	644	2.38	0 131	0.264	0 273
110.5	1,775	760	2.34	0.000	0.00	

y and x are mole fractions of benzene.

The same data may also be very simply obtained by a graphical construction illustrated in Fig. XII.6. On a px diagram, draw straight lines from the point 0 to the vapor pressure of pure toluene on the $x = 0$ ordinate at any chosen temperature. (OD is such a line.) Then from these points draw straight lines to the vapor pressures of pure benzene on the $x = 1$ ordinate (line DE, for example). These latter lines give the vapor pressure of all mixtures at a given temperature. The composition of the liquid boiling at any temperature is obtained by dropping a perpendicular from the intersection of the 760-mm. abscissa with the vapor-pressure line for that temperature (AC for $t = 95$°C.). The vapor composition is given by $AB/760 = \frac{488}{760} = 0.640$.

Referring to the tabulated data, it will be noted that p_B/p_T or α varies only from 2.64 to 2.34. Using an average value of $\alpha = 2.49$ in Eq. (XII.1), the values of y in column 7 were obtained, and it is seen that they agree closely with those in column 6 based on a variable α. This use of Eq. (XII.1) with an average α provides a very convenient formulation for yx data at constant pressure and a sufficiently accurate one for many purposes.

Nonideal Solutions.—The ideal solution, as we have emphasized before, is only a limiting case to which all actual solutions approach more or less closely, depending on conditions and on the particular system. Binary solutions that deviate markedly from the ideal may be classified into four different types, according to the form of their isothermal px
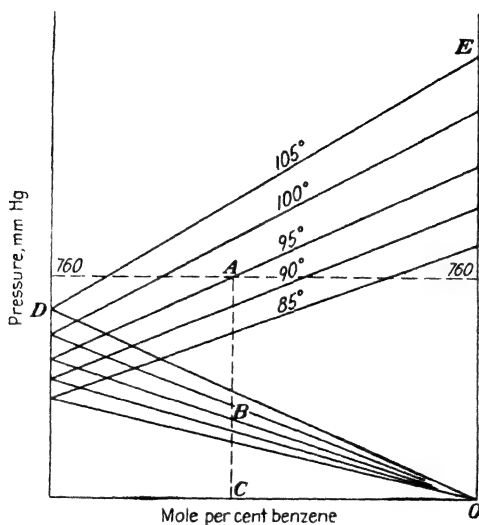
FIG. XII.6.—Determination of liquid-vapor equilibrium data for the system benzene-toluene at a total pressure of 1 atm.
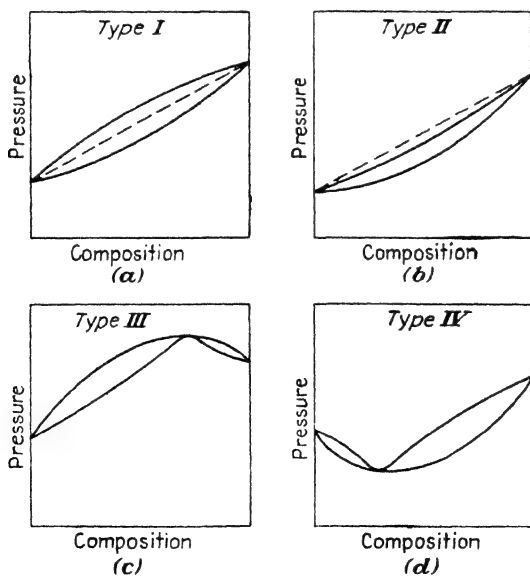
FIG. XII.7.—Pressure-composition diagrams of solutions that are not ideal.

diagrams as shown in Figs. XII.7a, b, c, and d.[1]   In all these diagrams, the upper curve is the liquid, or boiling-point, line and the lower the vapor, or dew-point, line.   Types I and II are often classed together, but there is a distinct difference in that I calls for vapor pressures of the solution that are greater than the ideal and in II they are less than the ideal (the dashed line represents the ideal solution).   Types III and IV are then seen to be merely extreme cases of I and II, respectively, in
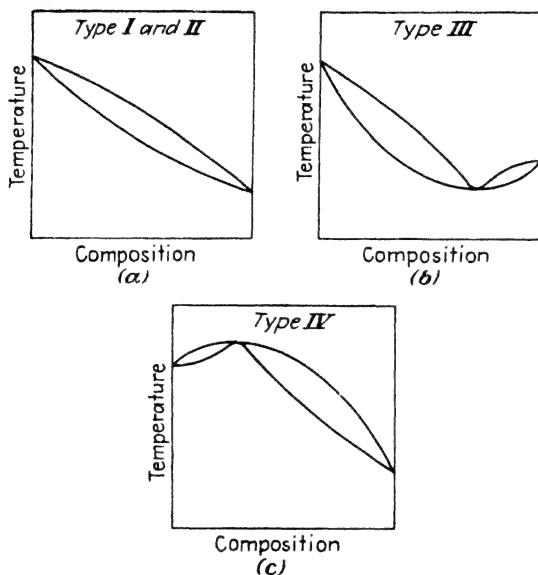
Fig. XII.8—Different types of temperature-composition diagrams.

which the deviations from the linear vapor-pressure relationship are so great that the vapor pressure must inevitably pass through a maximum or a minimum, respectively.   Typical systems representative of these four types are the following ones at temperatures near the normal boiling points:

I	II	III	IV
Oxygen–nitrogen	Chloroform–ethyl ether	Water–ethyl alcohol	Water and certain acids
Ethyl alcohol–ethyl ether	Chloroform–ben-zene	Carbon disulphide–acetone	Chloroform–acetone

[1] In all except a very few cases, we shall adopt the convention of basing composition on the component that has the higher vapor pressure or the lower boiling point.

Benzene–cyclohexane[1] is an especially interesting example of type III in that the two components have nearly the same vapor pressure and the deviation from the ideal solution is not great.   Thus we have the unusual case of a maximum vapor pressure in a nearly ideal solution.

The corresponding temperature-composition (tx) and vapor composition–liquid composition (yx) diagrams at constant pressure are shown in Figs. XII.8a, b, and c and XII.9, respectively.   On both these diagrams, types I and II are indistinguishable from each other and also from the ideal solution.   Type III, which exhibited a maximum vapor pressure on the px diagram, shows a minimum boiling point on the tx diagram, and vice versa for type IV.

Examination of either the px or the tx diagrams shows that, at a maximum or minimum in either curve, the vapor and liquid phases are identical in composition and hence behave as a pure component. This has a very important bearing on the separation of liquids by distillation, as we shall see later (page 594). A mixture that corresponds to a maximum or minimum in the boiling-point curve is known as an "azeotropic mixture" or an "azeotrope." The term is also applied by some authors to a mixture in which there are two liquid phases, because such a system would distill unchanged in composition just as the azeotrope in a one liquid-phase system.   Since

Fig. XII.9.—Different types of yx diagrams at either constant pressure or constant temperature.

on the yx diagram the diagonal represents points of identical composition in both phases, the curves for types III and IV will cross the diagonal at the composition corresponding to the maximum or minimum.   The diagonal can also be thought of as representing the relation between liquid and vapor compositions of mixtures of liquids so nearly alike that they behave as a single component, such as stereoisomers and most isotopic compounds.

Effect of Pressure.—So far we have considered only cases where the pressure on the system was substantially atmospheric.   It is of interest, and also important for certain applications, to consider briefly what happens when the pressure is changed.   (We are taking pressure rather than temperature as the independent variable because most distillations

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[1] SCATCHARD, G., S. E. WOOD, and J. M. MACHEL, *J. Phys. Chem.*, **43**, 119–130 (1939).

are conducted at constant pressure.)   Data in this field are very meager, but Fig. XII.10 represents the effect of pressure on the system oxygen-nitrogen,[1] one of the few that had been investigated until quite recently when several investigations on hydrocarbon systems were published.
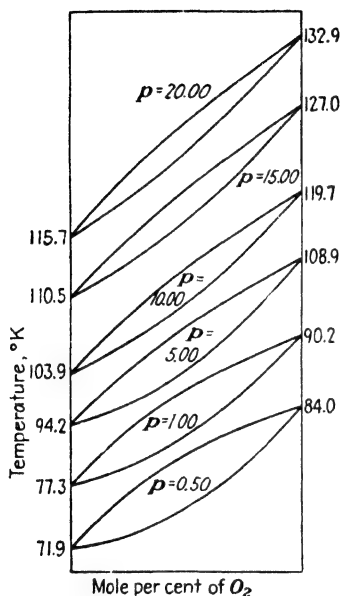
Fig. XII.10.—Isobars for the liquid and vapor phases of the oxygen-nitrogen system. Pressures are in atmospheres.

The chief effect of an increase in pressure is a decrease in the spread of composition between the liquid and vapor phases.   This is a general trend that would be expected from the fact that as the pressure (and hence the temperature) is increased one approaches more closely to the critical region; just by analogy to the behavior of a pure substance, one would expect to find a critical point for a mixture of given composition, and at this point the two phases would become identical.   This and other critical phenomena will be discussed more fully in the next section.

Another important effect of pressure is on the composition of an azeotrope. Since the latter behaves in distillation like a single component, some authors have adopted the theory that they represented actual chemical compounds of the two components.   There are practically no definite facts to support this view, and one strong argument against it is the fact that the azeotropic composition shifts continuously with

TABLE XII.1.—EFFECT OF PRESSURE ON THE COMPOSITION OF AN AZEOTROPE

Pressure, mm. Hg.	Boiling point of azeotrope, °C.	Mole per cent ethanol in azeotrope
100	34.2	99.6
150	42.0	96.2
200	47.8	93.8
400	62.8	91.4
760	78.1	90.0
1,100	87.8	89.3
1,450	95.3	89.0

[1] DODGE, B. F., and A. K. DUNBAR, *J. Am. Chem. Soc.*, **49**, 591 (1927).   DODGE, B. F., *Chem. Met. Eng.*, **35**, 622 (1928).

change in pressure or temperature. Table XII.1 illustrates the effect of pressure on the ethyl alcohol–water azeotrope.[1]

Critical Phenomena.—The critical point of a pure substance has the three following characteristics:

1. The liquid and vapor phases are identical.

2. The temperature is the maximum at which the two phases can co-exist.

3. The pressure is the maximum at which the two phases can coexist.

In the case of binary solutions these three phenomena no longer appear at one point but are exhibited at three separate points. This can best be shown on a pressure-temperature diagram such as is given in Fig. XII.11. This represents a section cut through a pressure-temperature-composition surface by a plane of constant composition. It consists of two boundary curves—one for liquid and one for vapor of the same composition—enclosing the field in which two phases can coexist, which meet at the critical point C, where the two phases become identical. This point is the point of tangency of the boundary curve and an envelope curve AB that joins the critical points of the two pure components. Point C' is the maximum temperature at which a vapor of this particular composition can be condensed to a liquid or the maximum temperature

Fig. XII.11.—Pressure–temperature diagram at constant composition for a binary solution in the critical region.

at which the two phases can coexist in a system of this particular total composition. This point, commonly known as the "cricondentherm" (critical condensation temperature), exhibits characteristic 2 of the critical point of a pure substance. Point M exhibits characteristic 3 since it is the maximum pressure at which a system of the given composition can exist in two phases.[2] The curve DMC is most easily visualized as the vapor-pressure curve of this particular mixture. Similarly, $EC'C$ is the locus of the dew points at a series of pressures. It is interesting to note that, whereas the vapor pressure of a pure substance always increases with the temperature, in the case of a binary solution it may

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[1] Data from the International Critical Tables, McGraw-Hill Book Company, Inc., New York.

[2] This point has been given no name but by analogy to the cricondentherm point it might be called a "cricondenbar."

rise to a maximum and then actually decrease as the temperature is increased in the vicinity of the critical point.

Figure XII.11 is for a single composition. To represent composition as a variable one could use a system of three coordinates and obtain a solid figure containing a *ptx* surface. In order to represent, at least partly, all three variables on a plane surface, we can adopt the usual expedient of taking a number of sections through this surface at constant composition and projecting the resulting curves all onto one plane as illustrated by Fig. XII.12. Typical systems exhibiting the behavior illustrated in this figure are CO_2-SO_2* and ethane-heptane.† Curves 1 and 7 are the vapor-pressure curves of the two pure components, and the others are the typical curves for a mixture with a vapor and a liquid branch. The points where the vapor branch of one curve intersect the liquid branch of another represent coexisting phases in equilibrium (point A, for example). It is clear that this must be so from the fact that a liquid and vapor phase at the same pressure and temperature must be in equilibrium. Curve $C_A C_B$ is the envelope curve joining the critical points of the two pure components, and it is the locus of the critical points of the mixtures. It will be designated the "critical curve." The form of this curve shown in Fig. XII.12 is one of the

Fig. XII.12.—Pressure-temperature curves at constant composition for a binary system. 1 and 7 are for the pure components, 2 to 6 are for different compositions, C equals the critical point, C' equals the cridondentherm point, M equals the cricondenbar point.

commonest, but not the only one that has been observed. Cases have been investigated in which the critical curve exhibits a maximum and also a minimum with respect to the temperature.

Figures XII.13 to XII.15 show the *px*, *tx*, and *yx* curves, respectively, for the type of system depicted on the *pt* diagram in Fig. XII.12. In Fig. XII.13, in diagram I the temperature is below the critical of either pure component; in II and III, it is above the critical temperature of the more volatile component but below that of the other component. Mixtures richer in component A than x_1 (diagram II) or x_2 (diagram III)

* CAUBET, F., *Z. physik. Chem.*, **40**, 257-367 (1902).
† KAY, W. B., *Ind. Eng. Chem.*, **30**, 459-465 (1938).

can no longer form two phases. In Fig. XII.14, diagram I, the critical pressure is below that of either component; in II it is above that of the less volatile one; in III, above the critical pressures of both components. Corresponding curves on the yx diagram at constant pressure are shown in Fig. XII.15.
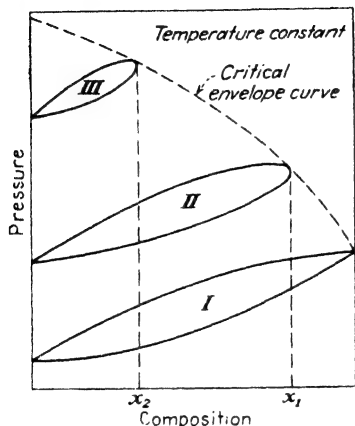
FIG. XII.13.—Pressure-composition curves in the critical region.
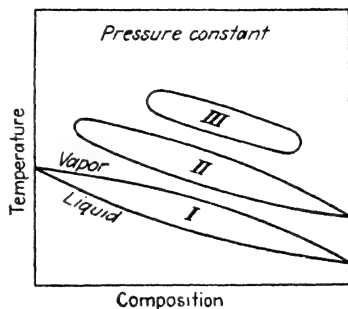
FIG. XII.14.—Temperature-composition curves in the critical region.
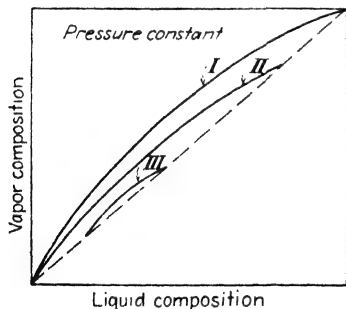
FIG. XII.15.—yx curves in the critical region.
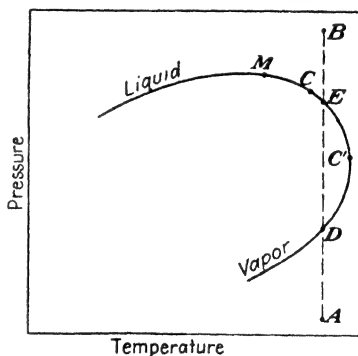
FIG. XII.16.—Retrograde condensation.

A very interesting phenomenon takes place when a mixture whose composition lies between that of the critical point and of the cricondentherm point is isothermally compressed. In Fig. XII.16, which is an enlargement of the critical region in Fig. XII.11, line AB represents an isothermal compression at constant total composition, starting with a vapor at A. At D the dew-point line is reached; and as compression is continued, the amount of liquid at first increases, then passes through a

maximum and decreases, and finally disappears altogether as the dew-point line is reached again at E. Further compression will produce no separation into two phases. This phenomenon is known as "retrograde condensation" and was first reported by J. P. Kuenen in 1892.

The change in the relative amount of the two phases is more easily visualized on the px diagram (Fig. XII.17) because any vertical line through the two-phase region cuts the horizontal tie lines into segments whose lengths are proportional to the amounts of the phases (see Chap. XIII, page 598, for proof). Thus, for example, HG/FH equals the ratio of the mass of liquid to the mass of vapor. At D this ratio is zero
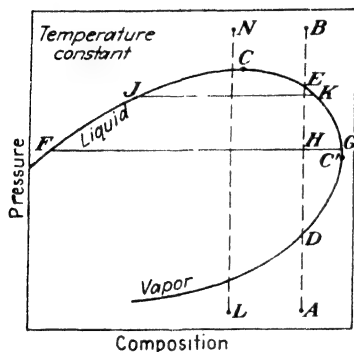
FIG. XII.17.—Retrograde-condensation illustrated on a pressure-composition diagram. C = critical point, C' = cricondentherm point.
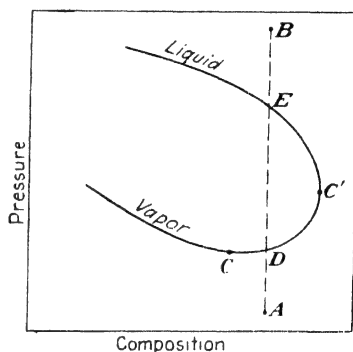
FIG. XII.18.—Retrograde condensation of the second kind. C = critical point, C' = cricondentherm point.

and again at E. Between these two points it obviously passes through a maximum.

At any composition to the left of that of the critical point C, the condensation phenomena are of the ordinary type, i.e., the liquid phase first formed at the dew point continues to increase until the whole system is liquid at the bubble point. This may be seen by considering the path LN.

When the relative position of the points C and C' is as indicated in Fig. XII.18, we have the peculiar situation that the line of isothermal compression $ADEB$ now reaches the liquid line at D and the phase which separates would ordinarily be regarded as a vapor phase.[1] As compression proceeds, this would increase in amount, pass through a maximum, and then decrease to zero at E when the liquid line is again crossed. This

[1] In the critical region there is no clear-cut distinction between a liquid and a vapor phase, and in the homogeneous region above the critical point there is no difference at all. In the critical region it might be better to refer to the two phases as the "less dense" and the "more dense" phase.

phenomenon was predicted by Kuenen[1] and called by him "retrograde condensation of the second kind," but it has never been observed though the relative position of points C and C' that would demand it is known.

Similar phenomena would be predicted for an isobaric process by using either the pt or the tx diagrams except that in this case the composition would be one lying between those of points C and M (Fig. XII.11) and the type of retrograde condensation would depend on the relative position of these two points.

Until very recently the phenomenon of retrograde condensation was considered to be only of academic interest and to have no relation to anything of practical value. This has been rather dramatically changed by the development of some processes for the recovery of petroleum from wells, involving the use of retrograde condensation. In some deep wells where high temperatures prevail the oil exists primarily in the vapor state at pressures of the order of 1,500 to 3,000 lb. per sq. in. When the pressure is reduced, liquid condenses (retrograde condensation is involved here because, although condensation is due both to a pressure and a temperature decrease, a considerable proportion of it would occur in an isothermal expansion) and is recovered as product. The residual gas is then compressed and recycled to the well in order to maintain the pressure, for if the pressure were allowed to decrease, the oil would condense in the well and be absorbed in the sands, from which it could not be recovered. For further details see papers by Katz and Kurata,[2] Katz and Singleterry,[3] and De Back.[4]

QUANTITATIVE TREATMENT OF NONIDEAL SYSTEMS

The general equations for phase equilibria in a binary system were developed in Chap. IV. We shall now proceed to apply a few of these equations to the types of systems that are of interest in distillation.

Konowalow's Laws.—First we shall make one or two very general deductions using Eqs. (IV.138) and (IV.139) in the following special forms applicable to the case of constant temperature:

$$\Delta v_2 \, dp = (y - x) \frac{\partial^2 F_L}{\partial x^2} \, dx \tag{XII.6}$$

$$\Delta v_1 \, dp = (x - y) \frac{\partial^2 F_V}{\partial y^2} \, dy \tag{XII.7}$$

where Δv_1 and Δv_2 are abbreviations for the dp coefficients in Eqs. (IV.138) and (IV.139), respectively.

[1] Kuenen, *op. cit.*, p. 64.

[2] Katz, D. L., and F. Kurata, *Ind. Eng. Chem.*, **32**, 817 (1940).

[3] Katz, D. L., and C. D. Singleterry, *A.I.M.E. Tech. Pub.* 971 (1938).

[4] De Back, E. E., *Petroleum Eng.*, **10**, 141 (1939).

Dividing Eq. (XII.6), by Eq. (XII.7),

$$\frac{\Delta v_2}{\Delta v_1} = - \frac{\partial^2 F_L/\partial x^2}{\partial^2 F_V/\partial y^2} \frac{dx}{dy} \tag{XII.8}$$

As long as the state is well removed from the critical region, then one can write as approximations

$$\Delta v_2 = v_V \tag{XII.9}$$
$$\Delta v_1 = -v_V \tag{XII.10}$$

It has been shown[1] from a consideration of the necessary condition for equilibrium at constant pressure and temperature that

$$\frac{\partial^2 F}{\partial x^2} \text{ or } \frac{\partial^2 F}{\partial y^2} > 0 \tag{XII.11}$$

Therefore, it follows that $\dfrac{dx}{dy} > 0$ (XII.12)

or an increase in the concentration of a component in one phase always causes an increase in the concentration of that same component in the other phase.

In similar fashion one can predict that the addition to the system of that component which is present in the vapor to a greater extent than in the liquid $(y > x)$ will cause an increase in the pressure. These are rules of general application except in the neighborhood of the critical region where it would not be expected to hold since Eqs. (XII.9) and (XII.10) are no longer true.

From Eqs. (XII.6) and (XII.7), $\dfrac{dp}{dx} = \dfrac{y - x}{\Delta v_2} \dfrac{\partial^2 F_L}{\partial x^2}$ (XII.13)

and $\dfrac{dp}{dy} = \dfrac{x - y}{\Delta v_1} \dfrac{\partial^2 F_V}{\partial y^2}$ (XII.14)

When $y = x$, $\dfrac{dp}{dx} = \dfrac{dp}{dy} = 0$ (XII.15)

In other words, wherever the vapor and liquid compositions are equal, there must be maxima or minima in the px or py curves (see Fig. XII.7), and vice versa.

These three rules are generally known as "Konowalow's laws," and they have proved useful in establishing the general trends of the isothermal equilibrium curves.

Duhem Equation.[2]—This equation, several forms of which were derived in Chap. IV, is most frequently written in one of the two following forms

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[1] KUENEN, *op. cit.*, pp. 28–31.

[2] Some authors prefer to call this the Gibbs-Duhem equation. There is considerable justification for this, since it is only a special case of the general equations of Gibbs.

applying only to isothermal systems when the vapor is an ideal gas:

$$x d \ln \bar{p}_A + (1 - x) d \ln \bar{p}_B = 0 \qquad \text{(XII.16)}$$

$$\frac{d \ln p}{dy} = \frac{y - x}{y(1 - y)} \qquad \text{(IV.167)}$$

Integration of either of these equations should yield a relationship from which vapor compositions could be calculated if liquid compositions were known as a function of pressure at constant temperature. This is an important result because the measurement of the vapor pressures of a series of liquid mixtures is generally much simpler than the determination of the composition of the equilibrium vapor.

Margules[1] suggested the following solutions for Eq. (XII.16):

$$\bar{p}_A = p_A x e^{\frac{\alpha_2}{2}(1 - x)^2 + \frac{\alpha_3}{3}(1 - x)^3 + \cdots} \qquad \text{(XII.17)}$$

$$\bar{p}_B = p_B (1 - x) e^{\frac{\beta_2}{2}x^2 + \frac{\beta_3}{3}x^3 + \cdots} \qquad \text{(XII.18)}$$

These may also be written

$$\ln \gamma_A = \frac{\alpha_2}{2}(1 - x)^2 + \frac{\alpha_3}{3}(1 - x)^3 + \cdots \qquad \text{(XII.19)}$$

and

$$\ln \gamma_B = \frac{\beta_2}{2}x^2 + \frac{\beta_3}{3}x^3 + \cdots \qquad \text{(XII.20)}$$

where γ is the activity coefficient. Applying the Duhem equation, one finds the following relations among the constants

$$\beta_2 = \alpha_2 + \alpha_3$$
$$\beta_3 = -\alpha_3$$

The constants α_2 and α_3 (or more if desired) can be determined from the px data. Zawidski[2] applied Eqs. (XII.17) and (XII.18) using only the two constants α_2 and α_3, which were determined from the slope of the px curve at the two ends where $x = 0$ and 1, respectively, and obtained a fairly good agreement with his own experimental measurements. The equations for this purpose are

$$\frac{\alpha_2}{2} + \frac{\alpha_3}{3} = \ln \left[\left(\frac{\partial p}{\partial x} \right)_{x=0} + p_B \right] - \ln p_A \qquad \text{(XII.21)}$$

and

$$\frac{\alpha_2}{2} + \frac{\alpha_3}{6} = \ln \left[p_A - \left(\frac{\partial p}{\partial x} \right)_{x=1} \right] - \ln p_B \qquad \text{(XII.22)}$$

Levy[3] devised two methods for using the Margules equations to calculate vapor compositions from measurements of total pressure as a function of liquid composition. Using only the first constant in the Margules

[1] MARGULES, M., *Sitzb. Akad. Wiss. Wien, Math. Naturw. Klasse*, **104**, 1243 (1895).
[2] ZAWIDSKI, J., *Z. physik. Chem.*, **35**, 129 (1900).
[3] LEVY, R. M., *Ind. Eng. Chem.*, **33**, 928 (1941).

series one gets

$$\ln \gamma_A = \alpha(1 - x)^2$$
$$\ln \gamma_B = \alpha x^2$$

If the solution were ideal, $\ln \gamma = \gamma - 1$, and using this as an approximation for solutions that do not deviate greatly from the ideal, one obtains the following equation equivalent to Levy's but in slightly different form

$$y = \frac{p_A}{p} x + \frac{p_A(1 - x) \Delta p}{p[p_A(1 - x) + p_B x]} \tag{XII.23}$$

where Δp is the difference between the actual total pressure and the calculated total pressure for an ideal solution.

For solutions that deviate considerably from the ideal, Levy retained the two constants of the Margules exponents and used the latter's method of evaluating them from the terminal slopes of the total pressure curve, except that he used an algebraic rather than a graphical method. Thus one readily obtains

$$\left(\frac{\partial p}{\partial x}\right)_{x=0} = \frac{p - p_B}{x}$$

and

$$\left(\frac{\partial p}{\partial x}\right)_{x=1} = \frac{p_A - p}{1 - x}$$

The use of these equations depends on a very accurate measurement of the total pressure of a solution in each of the two dilute regions and an equally accurate measure of the vapor pressure of the pure components. A direct determination of the pressure differences would be desirable and, indeed, almost essential to obtain the requisite accuracy.

Carlson and Colburn[1] made an extensive study of the Van Laar solutions of the Duhem equation and found them to represent the data well on many binary systems and to be more convenient to use than the Margules solutions. The Van Laar solutions are

$$\log \gamma_A = \frac{A}{\left[1 + \dfrac{Ax}{B(1 - x)}\right]^2} \tag{XII.24}$$

$$\log \gamma_B = \frac{B}{\left[1 + \dfrac{B(1 - x)}{Ax}\right]^2} \tag{XII.25}$$

whence

$$A = \log \gamma_A \left[1 + \frac{(1 - x) \log \gamma_B}{x \log \gamma_A}\right]^2 \tag{XII.26}$$

$$B = \log \gamma_B \left[1 + \frac{x \log \gamma_A}{(1 - x) \log \gamma_B}\right]^2 \tag{XII.27}$$

A and B are constants at a given temperature.

[1] CARLSON, H. C., and A. P. COLBURN, *Ind. Eng. Chem.*, **34**, 581 (1942).

When $\quad x = 0 \quad \log \gamma_A = A \quad \log \gamma_B = 0 \quad \gamma_B = 1.0$

$\qquad\quad x = 1 \quad \log \gamma_A = 0 \quad \gamma_A = 1.0 \quad \log \gamma_B = B$

Since, by definition,

$$\gamma_A = \frac{py}{p_A x} \quad \text{and} \quad \gamma_B = \frac{p(1 - y)}{p_B(1 - x)}$$

for an azeotrope where $y = x$,

$$\gamma_A = \frac{p}{p_A} \quad \text{and} \quad \gamma_B = \frac{p}{p_B}$$

Consequently we see that one may calculate the Van Laar constants A and B from azeotropic data and hence obtain the y, x equilibrium curve without the necessity of any other composition data.

Carlson and Colburn give the following procedure for obtaining y, x data from total pressure measurements:

From the definitions of the activity coefficients we may write

$$\gamma_A = \frac{p - \gamma_B p_B(1 - x)}{p_A x} \qquad\qquad \text{(XII.28)}$$

$$\gamma_B = \frac{p - \gamma_A p_A x}{p_B(1 - x)} \qquad\qquad \text{(XII.29)}$$

Putting into Eq. (XII.28) $\gamma_B = 1.0$, the value for $x = 0$, approximate values of γ_A are obtained and plotting $\log \gamma_A$ against x and extrapolating to $x = 0$, the terminal value is obtained, which we have already shown to equal A. In similar fashion the use of Eq. (XII.29) leads to B. These are first approximations to the correct values, and, by repeating the process using new values of γ_A and γ_B obtained from the approximate constants, one obtains a second set. These are generally close enough to the correct values, but further calculations may be desirable in some cases.

The $\log \gamma$ vs. x curves obtained from the Van Laar equations or from any other method of integrating the Duhem equation should also be useful for the smoothing and interpolation of experimental data in this field.

Lewis and Murphree[1] obtained vapor compositions from liquid compositions by an approximate stepwise integration of Eq. (IV.167). Over short ranges they assumed that the equilibrium yx relation could be represented by one of the two relations

$$x = a + by$$

or $\qquad\qquad\qquad\quad y = \dfrac{ax}{b + x}$

[1] Lewis, W. K., and E. V. Murphree, *J. Am. Chem. Soc.*, **46**, 1–7 (1924).

By using the linear relation, Eq. (IV.167) is readily integrated between limits of x_1, y_1, p_1, and x_2, y_2, p_2, to give

$$(1 - a - b) \log \frac{1 - y_1}{1 - y_2} - a \log \frac{y_2}{y_1} = \log \frac{p_2}{p_1} \qquad \text{(XII.30)}$$

and

$$a = x_1 - \frac{x_2 - x_1}{y_2 - y_1} y_1$$

$$b = \frac{x_2 - x_1}{y_2 - y_1}$$

Starting from an initial point x_1, y_1, p_1, where the vapor composition is known such as the point where $x_1 = y_1$ (pure component or constant boiling mixture), y_2 can be solved for by trial and error, given x_2 and p_2. Then this point can be used as the starting point for the next step, etc. In this way, the whole range of composition can be covered, preferably starting at the two ends and working both ways. The method was tested on four common binary solutions of organic liquids and good agreement obtained with the experimentally determined vapor compositions. The method is rather tedious and probably offers no advantage over other methods that are simpler to use.

Empirical Relations.—In Chap. IV we obtained the general equation (for the case where the vapor is an ideal gas)

$$\frac{y}{1 - y} = \frac{x}{1 - x} e^{\frac{\partial \pi}{\partial x}} \qquad \text{(IV.169)}$$

Now assume that the function π can be related to the liquid composition by the power-series relation

$$\pi = a + bx + cx^2 + dx^3 + \cdots$$

Then

$$\frac{\partial \pi}{\partial x} = b + 2cx + 3dx^2 + \cdots$$

and

$$\frac{y}{1 - y} = \frac{x}{1 - x} e^{b + 2cx + 3dx^2 + \cdots} \qquad \text{(XII.31)}$$

This is a useful empirical relationship for algebraic representation of yx data. For the special case where c and d are very small, Eq. (XII.31) reduces to

$$\frac{y}{1 - y} = \alpha \frac{x}{1 - x} \qquad \text{(XII.32)}$$

where α is an empirical constant. For the special case of ideal solutions, it was previously shown that

$$\alpha = \frac{p_A}{p_B}$$

In general, the quantity α, as defined by Eq. (XII.32), is very nearly a

constant for either an isotherm or isobar in the case of solutions that do not depart greatly from the ideal.   For example, Dodge[1] showed that the isobaric data of Dodge and Dunbar[2] on the system oxygen–nitrogen could be fairly well represented by Eq. (XII.32) with the following values for α:

p, atm...............	0.50	1.00	5.00	10.00	15.00	20.00
α (based on mole fraction of O_2).........	0.2027	0.2478	0.3798	0.4681	0.5292	0.5750

By representing α as a function of pressure either as an empirical equation or as a graph, one has a simple method of relating the liquid and vapor composition at any pressure in this range with sufficient accuracy for engineering purposes.

Two relations that have apparently proved useful for special cases are

$$\frac{y}{1-y} = k \left(\frac{x}{1-x}\right)^n \qquad (XII.33)[3]$$

and

$$\log \frac{py(1-x)}{p(1-y)x} = \frac{dp}{dx} \frac{\log p_A/p_B}{p_A - p_B} \qquad (XII.34)[4]$$

Equation (XII.33) is used to represent experimental yx data, but no theoretical deductions should be based on it, for it is in conflict with the Duhem equation.   Equation (XII.34) can be used to calculate vapor compositions, given the vapor pressure of the liquid as a function of concentration.   According to its authors it permitted very accurate calculations in several cases, but according to Lewis and Murphree it did not hold at all in at least one specific case.

Applications of the Duhem Equation.[5]—Most distillation calculations are dependent on liquid-vapor equilibrium data, and these must be reasonably accurate if the results are to be trusted.   Such data are difficult to secure, as is attested by the many inaccurate and discordant results in the literature, and hence it is important to have some means of checking their consistency.   This is the main field of usefulness of the Duhem equation.

[1] DODGE, *op. cit.*

[2] DODGE and DUNBAR, *op. cit.*

[3] LEHFELDT, R. A., *Phil. Mag.*, (5) **40**, 397 (1895).

[4] ROSANOFF, M. A., C. W. BACON, and J. F. W. SCHULTZE, *J. Am. Chem. Soc.*, **36**, 1993–2004 (1914).

[5] Much of the material in this section is based on papers by Beatty and Calingaert [*Ind. Eng. Chem.*, **26**, 904 (1934)] and by Carlson and Colburn [*Ind. Eng. Chem.*, **34**, 581 (1942)].

Isothermal Data.—Equation (XII.16) can readily be put in the form

$$\frac{d\bar{p}_A/dx}{\bar{p}_A/x} = \frac{d\bar{p}_B/d(1-x)}{\bar{p}_B/(1-x)} \tag{XII.35}$$

whose graphical interpretation is indicated in Fig. XII.19 in which partial-pressure curves for the system ethyl alcohol–chloroform[1] at 55°C. are plotted and the slopes called for by Eq. (XII.35) are indicated by
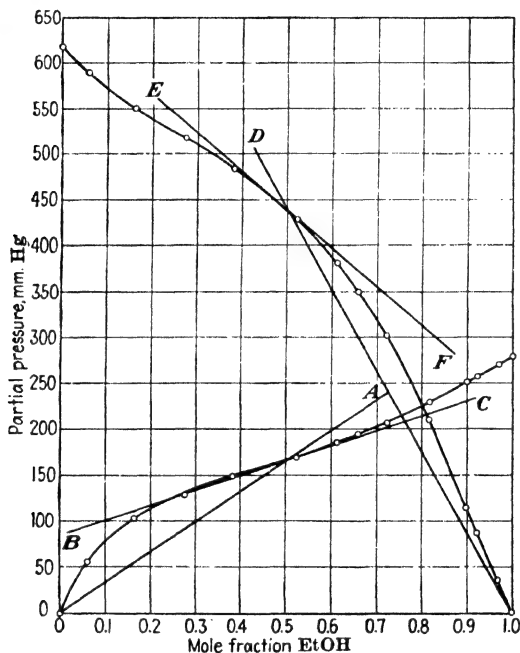
Fig. XII.19.—Test of vapor-liquid equilibrium data by the Duhen equation. [*Data of Scatchard and Raymond, J. Am. Chem. Soc.*, **60**, 1278 (1938), *for ethyl alcohol -chloroform solutions.*]

straight lines. Thus if the point where $x = 0$, $\bar{p} = 0$ is indicated by O and the point where $x = 1$, $\bar{p} = 0$ by O', we have

$$\frac{d\bar{p}_A}{dx} = BC$$

$$\frac{\bar{p}_A}{x} = OA$$

$$\frac{d\bar{p}_B}{d(1-x)} = EF$$

$$\frac{\bar{p}_B}{1-x} = O'D$$

[1] SCATCHARD, G., and C. L. RAYMOND, *J. Am. Chem. Soc.*, **60**, 1278–1287 (1938).

Evaluating the slopes for this particular system at $x = 0.50$, we find that Eq. (XII.35) is satisfied within the accuracy of graphical measurement of the slopes (about 1 per cent).   Therefore we can conclude that these equilibrium data are reliable provided that the vapor can be assumed an ideal gas.   Application of the Duhem equation in the form of Eq. (XII.35) involves the assumption of ideal gases, and hence it should always be borne in mind that failure of data to agree with this equation does not
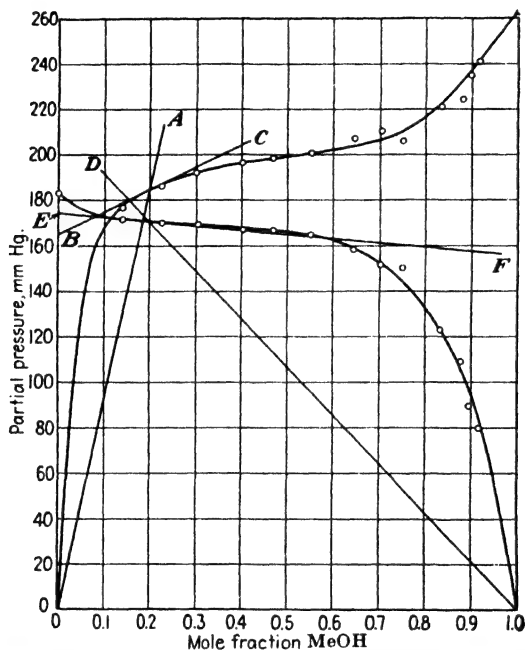
Fig. XII.20.—Use of Duhen equation to test vapor-liquid equilibrium data in methanol-benzene system at 40°C.   The point $p = 0$, $x = 0$ is designated by O in the text.   The point $p = 0$, $x = 1.0$ is designated by O' in the text.   [*From Lee, J. Phys. Chem.*, **35**, 3558 (1931).]

necessarily mean that the data are inaccurate.   When the pressure is 1 atm. or less, agreement within a few per cent may reasonably be expected unless there is association in the vapor state as in the case of formic or acetic acid vapors.

The data may also be tested by using the Duhem equation in the form

$$d \ln p = \frac{y - x}{y(1 - y)} \, dy \qquad \text{(IV.167)}$$

and integrating to determine p.   This is done graphically by plotting $(y - x)/y(1 - y)$ vs. y and measuring the area under the curve.   Scatch-

ard and Raymond made this test on their data and got very good agreement between calculated and observed pressures.

In Fig. XII.20 a test is made of the data by Lee[1] on methanol-benzene at 40°C. At $x = 0.20$ the slope ratio $BC/OA = \frac{191}{932} = 0.1095$ and slope ratio $EF/O'D = 0.0830$. By Eq. (XII.35) these two slope ratios should be equal. Since the two ratios do not agree and since both these vapors are substantially ideal gases at these low pressures, the conclusion is that the data are not very accurate.

Isobaric Data.—The Duhem equation was derived on the assumption of isothermal conditions and strictly applies only to isothermal data. This would appear to place a severe limitation on its usefulness since much of the liquid-vapor equilibrium data obtained for use in distillation calculations is isobaric. If, however, one uses the equation in the following form, derived in Chap. IV,

$$d \ln \frac{a_A}{x} = -\frac{1-x}{x} d \ln \frac{a_B}{1-x} \qquad \text{(IV.151)}$$

where a_A/x and $a_B/(1-x)$ are activity coefficients γ of components A and B, respectively, it is applicable to constant-pressure data without serious error. The reason for this is readily seen when we write

$$a_A = \frac{\bar{p}_A}{p_A}$$

and

$$a_B = \frac{\bar{p}_B}{p_B}$$

which is true when the vapor is an ideal gas and the standard state is that of the pure liquid component. Whereas the individual partial pressures and vapor pressures change considerably with temperature, the ratios change much more slowly and may be regarded as substantially constant over the relatively small temperature range involved in an isobaric distillation. Beatty and Calingaert[2] have demonstrated the validity of this assumption by showing that the isothermal data on the system carbon disulphide–acetone, at 35.2°C., and the isobaric data at 760 mm. ($t = 39$ to 54°C.) fall on practically identical curves when plotted as the activity coefficient vs. mole fraction; the curves are also in agreement with the requirements of Eq. (IV.151), showing that the agreement is not a fortuitous one.

Equation (IV.151) can also be expressed in the form

$$\frac{d \log \gamma_A}{dx} = -\frac{1-x}{x} \frac{d \log \gamma_B}{dx} \qquad \text{(XII.36)}$$

[1] Lee, S. C., *J. Phys. Chem.*, **35**, 3558–3582 (1931).
[2] *Loc. cit.*

and in this form it may be used to test isobaric data by means of the ratio of two slopes analogous to the use of Eq. (XII.35).

Typical activity coefficient curves may be readily calculated from the van Laar equations by choosing the values of A and B.   The set shown in Fig. XII.21 (taken from the paper by Carlson and Colburn) is based on $A = 1.13$ and $B = 0.49$, which gives a very good representation of the
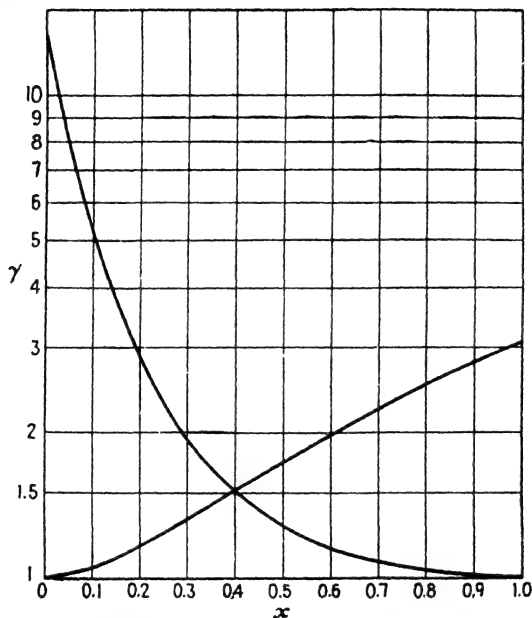
FIG. XII.21.—Activity coefficients vs. mole fractions calculated by van Laar equation. [From Carlson and Colburn, Ind. Eng. Chem., **34**, 583 (1942).]

data on the system: n-propyl alcohol, water at 1 atm.   By differentiation of the van Laar solutions we obtain

$$\left(\frac{\partial \log \gamma_A}{\partial x}\right)_{x=0} = -\frac{2A^2}{B}$$

$$\left[\frac{\partial \log \gamma_B}{\partial(1-x)}\right]_{(1-x)=0} = -\frac{2B^2}{A}$$

$$\left[\frac{\partial \log \gamma_B}{\partial(1-x)}\right]_{(1-x)=1} = 0$$

$$\left(\frac{\partial \log \gamma_A}{\partial x}\right)_{x=1} = 0$$

These equations are useful for indicating the trends of the curves at the terminal points.   The approach to the value of $\gamma = 1.0$ with a horizontal

tangent indicates that Raoult's law applies to the component whose mole fraction approaches 1.0, and Henry's law demands that the other end of each curve reach a finite value with a finite slope. When actual data are plotted in this way and are at variance with these requirements, there is qualitative evidence of inaccuracies in the data.

A plot of γ vs. x also shows at a glance the extent to which any binary solution departs from the ideal since for an ideal solution both curves would be horizontal lines at $\gamma = 1.0$.

TABLE XII.2.—CALCULATED RESULTS FOR TEST OF EQUILIBRIUM
DATA IN THE SYSTEM TOLUENE–N–OCTANE

Mole fraction toluene		Partial pressure, mm. Hg		Activity coefficient γ		Log of activity coefficient	
Liquid (x)	Vapor (y)	Toluene	Octane	Toluene	Octane	Toluene	Octane
0.0970	0.1640	125	635	1.177	0.988	0.0708	−0.0052
0.2030	0.2970	226	534	1.084	1.005	0.0350	+0.0022
0.3000	0.4100	312	448	1.066	1.011	0.0278	0.0048
0.3460	0.4605	350	410	1.063	1.016	0.0265	0.0069
0.4075	0.5265	400	360	1.060	1.014	0.0253	0.0060
0.4800	0.5855	445	315	1.036	1.048	0.0154	0.0204
0.5270	0.6235	474	286	1.028	1.070	0.0120	0.0294
0.5710	0.6620	503	257	1.028	1.083	0.0120	0.0346
0.6145	0.6975	530	230	1.023	1.099	0.0099	0.0410
0.6630	0.7300	555	205	1.014	1.143	0.0060	0.0581
0.7215	0.7785	592	168	1.010	1.153	0.0043	0.0618
0.7570	0.8030	610	150	1.003	1.196	0.0013	0.0777
0.7945	0.8325	633	127	1.003	1.212	0.0013	0.0835
0.8235	0.8555	650	110	1.000	1.229	0.000	0.0896
0.8580	0.8825	671	89	1.000	1.249	0.000	0.0966
0.9075	0.9225	701	59	0.999	1.283	−0.0004	0.1082
0.9450	0.9550	726	34	0.999	1.251	−0.0004	0.0973

Other qualitative deductions can be made from these curves plotted from experimental data. For example, the slopes of the lines must always be of opposite sign at a given value of x; if the slope of one of the curves is zero (a maximum or minimum) the other must also have a zero slope at the same value of x (except at the terminal points); if one component has γ values always greater than unity and has no maximum, the γ's for the other component must likewise be greater than 1.0. Also, when experimental data are plotted in this form, one can often see at a glance that the data are inaccurate in certain regions.

Illustration 4.—Examine and report on the accuracy of the published vapor-liquid equilibrium data for the system toluene–*n*–octane at 1 atm. [*Ind. Eng. Chem.*, **25**, 1136 (1933)].

Boiling points for this system were determined in a separate series of experiments. From a plot of these data the boiling temperatures corresponding to the various equilibrium compositions can be determined. It is then necessary to have vapor-pressure data for the pure components over the given boiling range. In this case
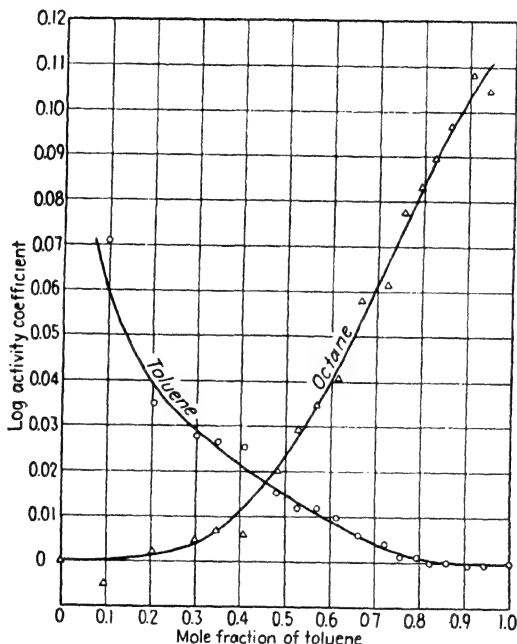
Fig. XII.22.—Test of liquid-vapor equilibrium data by the Duhem equation. [*Data of Bromley and Quiggle, Ind. Eng. Chem.*, **25**, 1136 (1933), *on toluene- n-octane.*]

use will be made of the equations developed by Beatty and Calingaert (*loc. cit.*). These are

Toluene, $\qquad\qquad\qquad \log p = 7.7309 - \dfrac{1,860.0}{T}$

n–Octane, $\qquad\qquad\quad \log p = 7.7503 - \dfrac{1,941.4}{T}$

where p is in millimeters of mercury and T in degrees Kelvin. Two series of liquid-vapor composition data were given, one based on analysis by density and the other on analysis by refractive index. To reduce the number of calculations and amount of material to be tabulated, only the density series is used in this illustration.

Partial pressures and activity coefficients were then calculated assuming the vapors to be ideal gases and the results tabulated in Table XII.2. The results are plotted in Fig. XII.22. Making a quantitative comparison of slopes by applying Eq. (XII.36) we find the following:

Mole fraction..........	0.25	0.50	0.75
Theoretical slope ratio $\left(= -\dfrac{1-x}{x} \right)$	-3.0	-1.0	$-\frac{1}{3}$
Actual slope ratio............................	-4.0	-0.40	-0.14

It is true that the slopes cannot be determined with high accuracy, but the large discrepancies revealed by these figures are sufficient to indicate that these data are not very accurate.

Activity-coefficient Curves by Graphical Integration.—To make a complete test of an isotherm or isobar over the whole composition range, Eq. (IV.151) may be graphically integrated and used to derive a set of consistent γ vs. x curves. This has the advantage over the integrations by means of such equations as those of Margules or van Laar that it is rigorous and does not leave one in an uncertainty as to whether the particular equation is applicable or not. The procedure is briefly indicated as follows:

Integrating Eq. (IV.151),

$$\ln (\gamma_A)_2 - \ln (\gamma_A)_1 = - \int_1^2 \frac{1-x}{x} d \ln \gamma_B \qquad (XII.37)$$

Take limit 1 at pure A where $x = 1$ and $\gamma_A = 1$. Then Eq. (XII.37) becomes

$$\ln \gamma_A = - \int_{x=1}^{x=x} \frac{1-x}{x} d \ln \gamma_B \qquad (XII.38)$$

At the other limit where $x = 0$, $\quad (\gamma_A)_2 = k_A \qquad$ (Henry's law)

and therefore the integral approaches a constant value, which is $\ln k_A$.

Similarly, $\qquad \ln \gamma_B = - \int_{x=0}^{x=x} \frac{x}{1-x} d \ln \gamma_A \qquad (XII.39)$

and at $x = 1$ the integral approaches the constant value $\ln k_B$.

With these two equations, either activity-coefficient curve may be calculated from the other by a graphical integration. For example, assume that the curve of γ_B vs. x may be temporarily fixed on the basis of experimental data. Plot $\ln \gamma_B$ as abscissa against $(1 - x)/x$ as ordinate, starting at $x = 1$ where $(1 - x)/x = 0$ and $\gamma_B = k_B$, a Henry law constant. As one approaches the other limit $(x = 0)$, $(1 - x)/x$ approaches ∞ but the integral nevertheless approaches a finite constant value, as shown above. The value of the integral up to any given x is of course the area under this curve, which is determined in any one of various ways.

One now has a consistent set of activity-coefficient curves that should agree with the experimental data if the latter are accurate. If there are

significant deviations, we have definite evidence of inaccuracies somewhere in the data. By relocating one of the activity-coefficient curves and recalculating the other by the above described procedure, it is possible with a few trials to arrive at a thermodynamically related pair of curves that best represent the data as a whole. This should provide one of the best ways of smoothing and correlating data on liquid-vapor equilibria either at constant temperature or constant pressure.

It should be noted in passing that the test of isobaric data requires accurate information on the vapor pressures of the two pure components over the temperature range involved. Lack of such data precludes the possibility of testing much of the data now available in the literature.

For further examples of the application of the Duhem equation in this field, reference should be made to the paper by Beatty and Calingaert.[1]

PARTIALLY MISCIBLE LIQUIDS

Many pairs of liquids of industrial importance, such as aniline-water, furfural-water, and phenol-water, belong in this class. If one starts with pure liquid A and adds small amounts of liquid B to it, keeping the temperature constant, at first B dissolves in A, forming only one liquid phase. As addition of B continues, a point is reached at which another liquid phase appears. From the phase rule we see that the system is now univariant and, with the temperature fixed, the state of the system is fixed; in other words, the pressure and composition of all three phases and properties of the phases are fixed. The liquid phases will be saturated solutions of one component in the other, and further addition of B will merely result in changing the relative amount of the two liquid phases. When the total composition of the whole liquid reaches that corresponding to a saturated solution of A in B, further addition of B results in the disappearance of that phase, which is a solution of B in A.

Critical-solution Temperature.—Observations similar to those just described would be made at other constant temperatures, but the composition of the two saturated solutions would vary with the temperature. In many cases, as the temperature increases the two liquid phases approach each other in composition and finally become identical, and above this temperature only one liquid phase exists. The temperature and composition at which this occurs is a "critical point" analogous to the critical point where liquid and vapor become identical in a one-component system or a binary system of completely miscible liquids. This behavior is represented graphically in Fig. XII.23, which shows how the composition of all three coexisting phases changes with the temperature. Since there is only one degree of freedom, it is clear that the pressure is not an independent variable but changes in a definite manner with the temperature.

[1] *Loc. cit.*

A typical example of a system that behaves in this manner is phenol-water.[1]   Mixtures of hexane and methyl alcohol give a similar diagram except that the vapor-phase composition is intermediate between those of the two liquid phases.   Aniline-water mixtures also give a diagram of this type with an upper critical temperature.

In the case of certain mixtures, for example, triethylamine and water, a critical point for the two liquid phases is reached when the temperature is lowered as shown in Fig. XII.24.[2]   The extremely rapid change in the solubility in both liquids as the critical point is approached is notable. The vapor curve is purely an assumed one since no data are available.
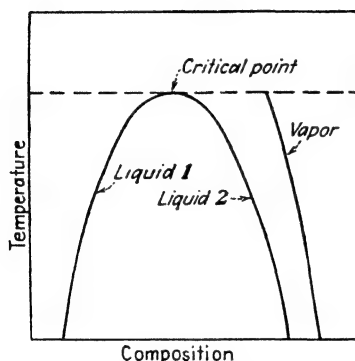
Fig.   XII.23.—Temperature-composition diagram for a three-phase system (two liquid and one vapor) with an upper critical temperature for the two liquid phases.
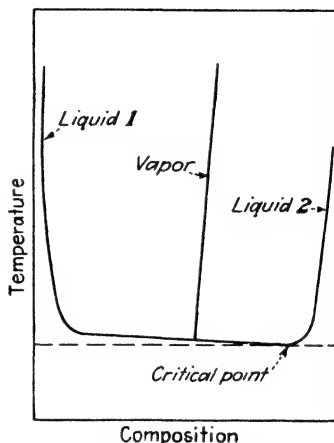
Fig. XII.24.—Temperature-composition diagram for a three-phase system (two liquid and one vapor) with a lower critical temperature for the two liquid phases.

Since systems with both upper and lower critical-solution temperatures were known, it was but natural to expect to find both in a given system if the observations were carried over a wide enough temperature range.   The result would be a diagram such as that shown in Fig. XII.25. Several systems that exhibit this behavior have been discovered, the classical one being that of nicotine − water.[3]   Probably all systems would show this type of behavior were it not for the fact that solid phases appear before the lower critical temperature is reached and a vapor-liquid critical point is reached before the upper critical point of the two liquids is attained.

[1] SCHREINEMAKERS, F. A. H., *Z. physik. Chem.*, **35**, 459–479 (1900).

[2] ROTHMUND, V., *Z. physik. Chem.*, **26**, 461 (1898).

[3] HUDSON, C. S., *Z. physik. Chem.*, **47**, 113–115 (1903).

In Fig. XII.26 is shown the type of diagram given by mixtures of ethyl ether and water,[1] in which the ether-rich solution becomes identical with
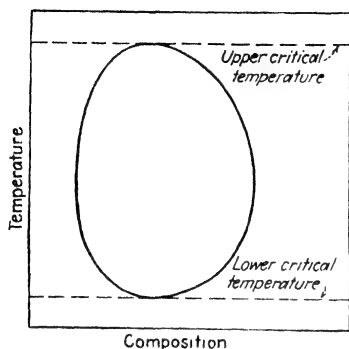
FIG. XII.25.—Temperature-composition diagram for a three-phase system (two liquid and one vapor) with both upper and lower critical temperatures for the two liquid phases.
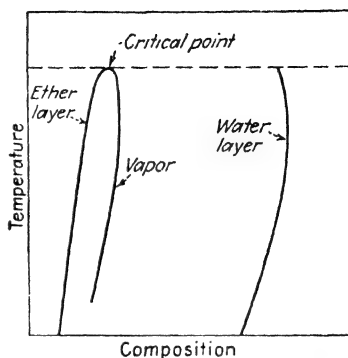
FIG. XII.26.—Temperature-composition diagram for a three-phase equilibrium in the system ethyl-ether-water.

the vapor at about 200°C. Another type of diagram that would be expected on general grounds is one with a lower liquid-liquid critical point and an upper liquid-vapor critical point, as illustrated in Fig. XII.27. This type of diagram is exhibited by mixtures of ethane and various aliphatic alcohols such as ethyl and propyl.

Typical Pressure-composition Diagrams.—In the distillation of systems involving partially miscible liquids, one is interested, not only in the three-phase equilibria, but the two-phase ones as well. In Figs. XII.28 to XII.30 are shown some of the typical pressure-composition (*px*) diagrams at constant temperature that have been observed. In Fig. XII.28, which represents a system such as aniline-water or furfural-water (case I) where the three-phase vapor pressure is greater than the vapor pressure of either component, the following equilibria are represented:

FIG. XII.27.—Temperature-composition diagram for a three-phase equilibrium in a system with a lower critical temperature for the liquid phases and another critical point for one liquid and the vapor phase.

AB = vapor-pressure curve of unsaturated liquid 2 (liquid rich in component B).

[1] KLOBBIE, E. A., *Z. physik. Chem.*, **24**, 615 (1897).

AC = composition of vapor in equilibrium with the liquid whose composition varies along AB. (Horizontal tie lines such as JK connect the liquid and vapor phases in equilibrium.)

ED = vapor-pressure curve of unsaturated liquid 1 (rich in A)
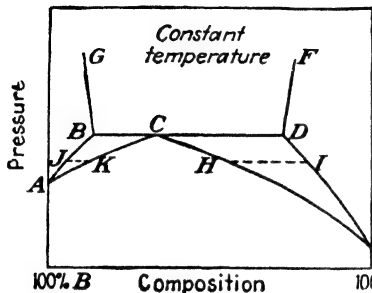
FIG. XII.28.—Pressure-composition diagram for a system containing two liquid phases and one vapor phase (Case I).
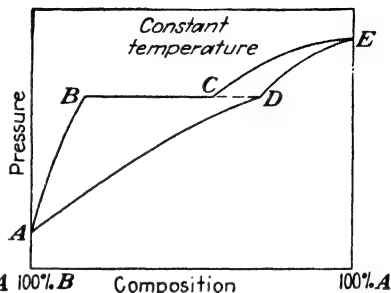
FIG. XII.29.—Pressure-composition diagram for a system containing two liquid phases and one vapor phase (Case II).

EC = vapor branch of this equilibrium between vapor and liquid 1. (HI is a tie line just like JK.)

Point B = B-rich solution saturated with A

Point D = A-rich solution saturated with B

All compositions of the total system lying between B and D will yield two liquid phases having the compositions represented by B and D and a vapor phase having the invariant composition of point C. BG and DF represent equilibrium between the two saturated liquids in the absence of a vapor phase. The slope of these lines depends on the volume changes in mixing the components. If mixing results in an increase in volume, then pressure will favor a lowered miscibility, as shown in Fig. XII.28, and vice versa. Generally, these two-phase liquid-liquid equilibria are not considered since they have little or no application to distillation. The effect of pressure on the degree of miscibility is too small to be of any practical consequence.
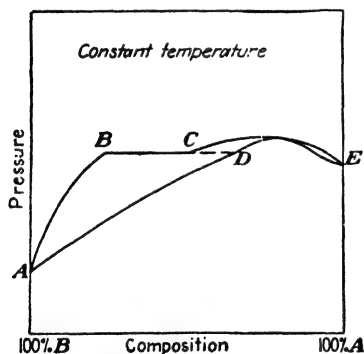
FIG. XII.30.—Pressure-composition diagram for a system containing two liquid phases and one vapor phase (Case III).

Figure XII.29 represents case II where the three-phase vapor pressure is intermediate between the vapor pressures of the two pure components. AB and CE are the vapor-pressure curves of the unsaturated liquids, and

AD and *DE* are the curves for the coexisting vapor phases. The saturated liquids represented at *B* and *C* are both in equilibrium with the vapor of composition corresponding to *D*. The usual horizontal tie lines would denote the compositions of the coexisting phases.

There may also be maxima or minima in the vapor-pressure curves of one of the unsaturated liquid phases. The case of a maximum (case III) is illustrated in Fig. XII.30. This type of behavior is exhibited by the important pair phenol-water.

Constant Pressure.—In the solution of distillation problems one is more directly concerned with behavior at constant pressure, and hence temperature-composition curves at constant pressure are more directly useful than the ones just given. Investigations on equilibria in the
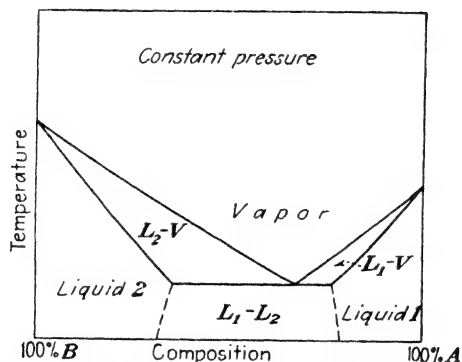
FIG. XII.31.—Temperature-composition diagram for a system containing a vapor phase and two liquid phases. *L₂* = liquid 2; *L₁* = liquid 1.

laboratory, however, are usually made at constant temperature, and the temperature-composition diagrams must then be constructed from the data for a series of pressure-composition ones. The temperature-composition diagram for mixtures like aniline and water corresponding to the *px* diagram of Fig. XII.28 is shown in Fig. XII.31. The various fields are clearly marked in the figure; no explanation appears to be necessary since *tx* and *px* diagrams are similar, the one being essentially an inverted replica of the other. Other *tx* diagrams may be drawn to correspond to the various *px* diagrams illustrated.

The relationship between the diagram of **Fig. XII.31** and corresponding diagrams for (1) completely miscible liquids (**Fig. XII.8b**) and (2) immiscible liquids (**Fig. XII.2**) is very interesting and is illustrated in **Fig. XII.32.** At the lowest temperature and pressure (p_1) the diagram approaches that of the pair of immiscible liquids where the two liquid phases are the pure components. As the temperature is raised, the two liquids approach each other, and we have the typical diagram for partially

miscible liquids.   When the pressure is p_4, the two liquids are completely miscible, and we have the typical minimum boiling-point type of diagram. At p_3 the constant-temperature line of the diagram has just reached the critical-solution temperature, and the two liquid phases are identical.

yx **Diagrams.**—Vapor composition–liquid composition, or yx, diagrams corresponding to the px diagrams shown in Figs. XII.28 (case I), XII.29 (case II), and XII.30 (case III) are illustrated in Fig. XII.33 as curves I, II, and III, respectively. The general form of this diagram is the same whether the pressure or the temperature is held constant.
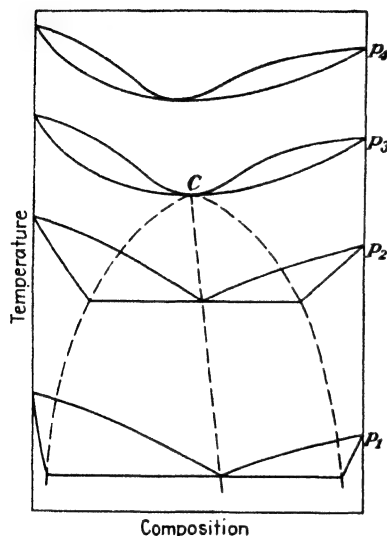
Fig. XII.32.—Relationship between tx diagrams for completely miscible and partially miscible liquids.
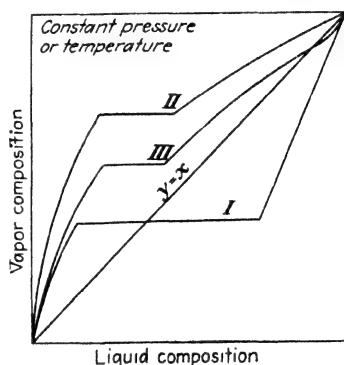
Fig. XII.33.—yx curves for systems of partially miscible liquids.

Application of the Simple Solution Laws.—Let A and B represent the two pure components and y and x the mole fractions of A in vapor and liquid, respectively.   Let us assume that the vapor pressure of the solvent in either of the two liquid phases is given by Raoult's law (ideal solution) and that of the solute by Henry's law.   These assumptions are, of course, only strictly correct at the two limits where $x \rightarrow 1$ and $x \rightarrow 0$, but they are approximately true as long as the solutions are fairly dilute.

Then, for the B-rich solution we have

$$\bar{p}_A = k_A x \qquad \text{(XII.40)}$$

$$\bar{p}_B = p_B(1 - x) \qquad \text{(XII.41)}$$

$$p = \bar{p}_A + \bar{p}_B$$
$$= k_A x + p_B(1 - x) \qquad \text{(XII.42)}$$

$$x = \frac{p - p_B}{k_A - p_B} \qquad \text{(XII.43)}$$

$$y = \frac{\bar{p}_A}{p}$$

$$= \frac{k_A x}{p} \tag{XII.44}$$

$$y = \frac{k_A}{p} \frac{p - p_B}{k_A - p_B} \tag{XII.45}$$

$$y = \frac{k_A x}{k_A x + p_B(1 - x)} \tag{XII.46}$$

Similarly, for the other, or A-rich, solution, one can readily derive

$$p = p_A x + k_B(1 - x) \tag{XII.47}$$

$$x = \frac{p - k_B}{p_A - k_B} \tag{XII.48}$$

$$y = \frac{p_A x}{p_A x + k_B(1 - x)} \tag{XII.49}$$

Since the partial pressures of A must be the same over the two saturated solutions and likewise for component B, we can write

$$k_A = p_A \frac{x_1}{x_2} \tag{XII.50}$$

and

$$k_B = p_B \frac{1 - x_2}{1 - x_1} \tag{XII.51}$$

where subscripts 1 and 2 refer to the A-rich and the B-rich saturated solutions, respectively.

Application of these equations is shown by the following numerical illustration.

Illustration 5.—At 110°C. a saturated solution of aniline in water contains 7.95 per cent aniline by weight, and a saturated solution of water in aniline contains 88.05 per cent aniline by weight. The vapor pressures of pure aniline and of water at 110°C. are 69.2 and 1,073 mm., respectively. Construct a *pxy* diagram for the mixture at 110°C.

The mole fractions of aniline in the two solutions are

$$\frac{(7.95/93.1)}{(7.95/93.1) + (93.1/18)} = 0.0162 \qquad \text{(water-rich solution)}$$

$$\frac{(88.05/93.1)}{(88.05/93.1) + (11.95/18)} = 0.587 \qquad \text{(aniline-rich solution)}$$

By Eq. (XII.50), $\qquad k_A = 69.2 \dfrac{0.587}{0.0162} = 2,510$

By Eq. (XII.51), $\qquad k_B = 1,073 \dfrac{0.9838}{0.413} = 2,560$

The total pressure for three-phase equilibrium is calculated from either Eq. (XII.42) or Eq. (XII.47).

By Eq. (XII.42), $\quad p = 2,510 \times 0.0162 + 1,073 \times 0.9838 = 1,097$

The px lines for the two unsaturated solutions are, by Eqs. (XII.42) and (XII.47), straight lines connecting the vapor pressure of the pure component with the three-phase pressure. Values of y calculated from Eqs. (XII.46) and (XII.49), respectively, for assumed values of x are tabulated below.

Water-rich solution		Aniline-rich solution	
x	y	x	y
0.001	0.00234	0.587	0.0371
0.005	0.0116	0.650	0.0478
0.010	0.0231	0.700	0.0593
0.015	0.0344	0.800	0.0977
0.0162	0.0371	0.900	0.196
		0.950	0.339
		0.975	0.517
		0.990	0.728

These results are plotted in Fig. XII.34 to give a pxy diagram for this system.[1] A txy diagram for the system at constant pressure could be obtained by plotting a series of the isothermal diagrams and reading off the values at the given constant pressure.

One might also write Eq. (XII.46) in the form

$$y = \frac{x}{x + (p_B/k_A)(1 - x)} \qquad \text{(XII.52)}$$

and similarly for Eq. (XII.49). The ratios p_B/k_A and k_B/p_A (analogous to the relative volatility α in the case of ideal solutions) should not change much with temperature, and by using an average value one could derive the yx diagram for constant pressure.

This method of obtaining the equilibrium data on systems of partially miscible liquids is recommended only as a first approximation in the absence of experimental data. There is considerable doubt about the general validity of the simple solution laws even for quite dilute solutions. Thus in the case of phenol-water the departure from this behavior is great according to the data of Sims,[2] which show a constant boiling mixture at 1 atm. and 1.90 mole per cent phenol in the water layer.

[1] Since this problem was solved, the data of Griswold, Andres, Arnett, and Garland [*Ind. Eng. Chem.*, **32**, 878 (1940)] have appeared. These investigators give the coexisting phase compositions for the aniline-rich solution at 100°C. Comparing their experimental data with those calculated by the method illustrated, it is found that, although the deviation from a linear p, x relation is considerable, the calculated p, y curve agrees closely with the experimental one.

[2] Reproduced in Walker, Lewis, McAdams, and Gilliland, "Principles of Chemical Engineering" (3d ed., McGraw-Hill Book Company, Inc., New York, 1937).
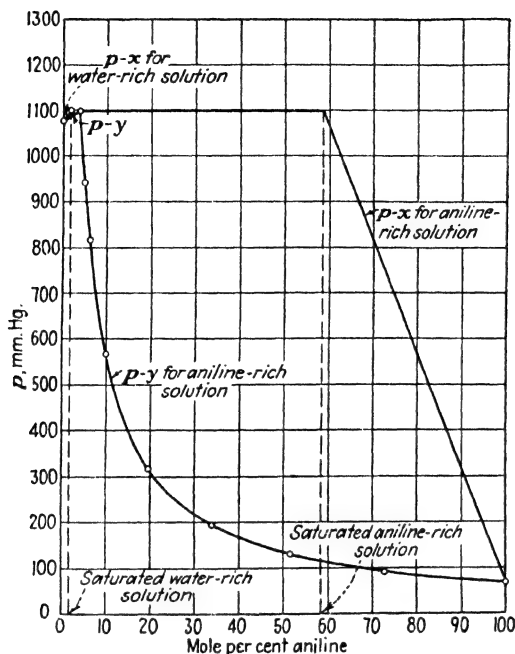
Fig. XII.34.—pxy diagram for aniline-water solutions at 110°C.
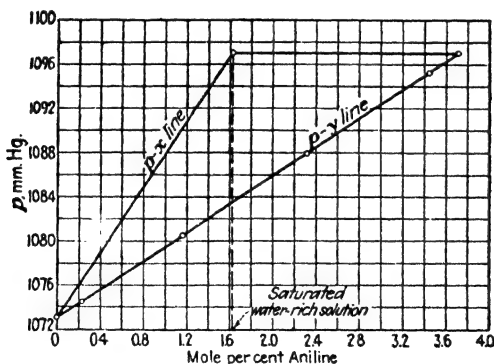
Fig. XII.34a.—Magnified pxy diagram for the water-rich phase. System: aniline-water at 110°C.

TERNARY SYSTEMS

The discussion will be limited to the case of completely miscible liquids. The graphical method of presentation, which was so useful for binary systems, is still possible in this case but considerably more

complex. When more than three components are to be treated, it must generally be abandoned altogether.

The composition of a three-component system is conveniently represented by means of an equilateral triangle, as shown in Fig. XII.35. This is possible because of the property of such a triangle that the sum of the perpendiculars to the three sides from any point is equal to the altitude (perpendicular from an apex to the opposite side). This is readily seen by drawing equidistant lines parallel to each of the sides of the triangle. These lines as drawn in Fig. XII.35 divide the altitudes into 10 equal parts. If we take any point such as p and draw the perpendiculars to the sides, we see that pf is 2 units long, pe 3 units, and pg 5 units,
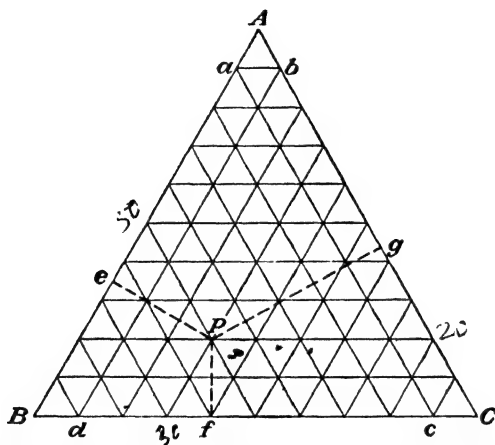
Fig. XII.35.—Representation of the composition of a ternary system.

giving the total of 10. If, then, the apexes A, B, and C represent 100 per cent of components A, B, and C, respectively, the lines parallel to the opposite bases represent 90 per cent, 80 per cent, etc., of the component marked at the respective apex. Thus ab represents all mixtures containing 90 per cent A, bd all mixtures containing 10 per cent C, and ac all mixtures containing 10 per cent B. The side AB would give the composition of a binary mixture of A and B and similarly for the other two sides of the triangle. The point p therefore corresponds to a mixture containing 20 per cent A, 50 per cent B, and 30 per cent C.

By erecting perpendiculars to the plane of this triangular diagram, another variable such as pressure or temperature can be represented, as shown in Fig. XII.36. Since any point within this prism corresponds to a system with three degrees of freedom and since a single-phase three-component system has four degrees of freedom, it is clear that some one variable must be specified as constant for the whole diagram; in this

case, the pressure is assumed constant.   At constant pressure there will
be two degrees of freedom when two phases coexist, and hence we shall
have a tx_Ax_B surface for the liquid phase and a ty_Ay_B surface for the vapor
phase.   These two surfaces are shown as $DGFJEH$ and $DKFMEL$,
respectively.   The compositions of any two coexisting phases could be
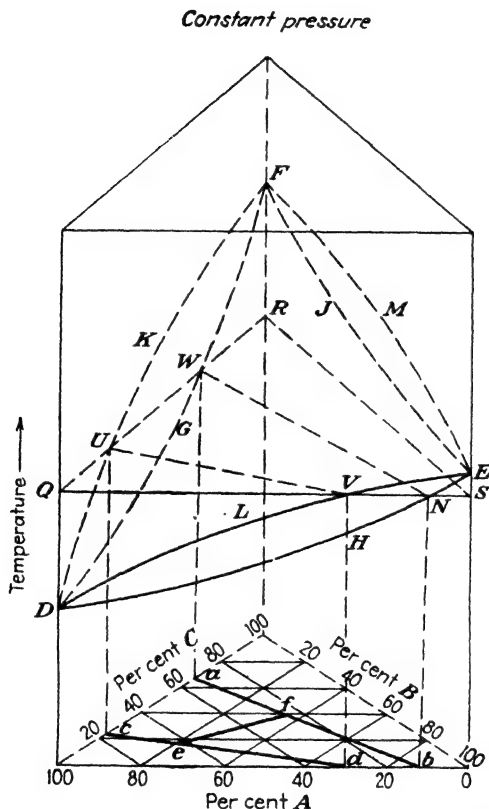
Fig. XII.36.—Temperature-composition diagram of a ternary system of completely
miscible liquids.

indicated by straight (tie) lines connecting these two surfaces, but these
would serve no useful purpose and would hopelessly complicate the figure.
The intersections of these two surfaces with the three vertical planes
forming the sides of the prism give the familiar lens-shaped txy diagrams
of the binary system.   Thus DHE is the intersection of the liquid surface
with the front vertical plane of the prism and represents the tx, or boiling-
point, curve of the binary system AB.   Similarly, DLE is the intersec-

tion with the vapor surface and hence is the *ty*, or dew-point, curve for the *AB* binary.

If one considers any plane parallel to the base of the prism such as *QRS*, this will intersect the two surfaces; the lines of intersection are shown as *WN* and *UV* for the liquid and vapor surfaces, respectively. These two lines, which are shown projected onto the base as *ab* and *cd*, represent the compositions of the phases that coexist at a *given p and t* since temperature is constant along any horizontal plane. They are not,
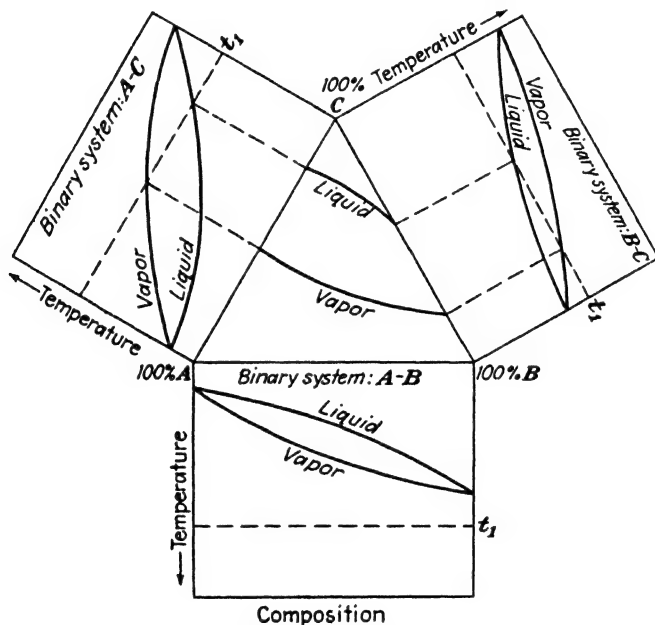
Fig. XII.37.—Phase diagram of a ternary system.

in general, straight lines but have been drawn so in the figure merely for convenience. To show the compositions of the two phases, tie lines can be used as shown by *ef*. From this line we see that a liquid of approximately 25 per cent *A*, 35 per cent *B*, and 40 per cent *C* is in equilibrium with a vapor of approximately 65 per cent *A*, 20 per cent *B*, and 15 per cent *C* at this particular pressure and temperature.

By rotating the three vertical planes of the prism 90 deg. around their respective base lines as axes so that they lie in the base plane, we obtain the diagram shown in Fig. XII.37, which is a convenient one for showing simultaneously the phase relationships in the three binaries as well as in the ternary system. This whole figure is at some constant pressure. The triangular diagram in the center represents a horizontal section

through the prism and hence is a constant-temperature as well as a constant-pressure plane. The particular temperature t_1 chosen in this case lies above the boiling points of both A and B. This is a plane at a higher temperature level than the one shown in Fig. XII.36, which lies above the boiling point of pure A but below that of B.

A yx diagram for ternary systems at a given p or t can be constructed as shown in Fig. XII.38. Any point in the triangle would correspond to some composition of the liquid (or vapor), and there would be two series of contour lines, one consisting of lines connecting all points having a given per cent A in the vapor (or liquid) and the other of lines of constant
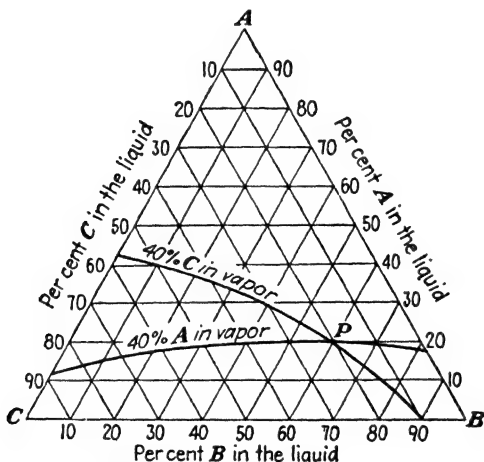
Fig. XII.38.—yx diagram for ternary systems.

per cent C in the same phase. Only one such line in each series is shown in the figure to prevent confusion. The intersection point p must correspond to a vapor containing 40 per cent A, 20 per cent B, and 40 per cent C. The equilibrium liquid, from the coordinates of the triangle, is seen to be 20 per cent A, 60 per cent B, and 20 per cent C.

Griswold and Dinwiddie[1] have presented vapor-liquid composition data for a ternary system by means of two diagrams with ordinary Cartesian coordinates. Such diagrams are somewhat easier to read than a triangular one.

The cases of ternary mixtures that have been illustrated are those in which no constant-boiling, or azeotropic, mixtures are formed. Such azeotropic mixtures are well known in ternary systems, a case of considerable industrial importance being the system ethyl alcohol–benzene–water, which is also complicated by the fact that at 1 atm. two liquid

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[1] GRISWOLD, J., and J. A. DINWIDDIE, *Ind. Eng. Chem.*, **34**, 1188 (1942).

phases are present.   The consideration of three-component systems with constant-boiling mixtures or with partial liquid miscibility is beyond the scope of this text.

For ternary mixtures which are ideal in the liquid phase and of which the vapor can be considered an ideal gas, the equilibrium relationships at constant temperature can be quite simply expressed by equations analogous to those used for binary systems.   Thus, if we express all compositions in terms of the mole fractions of components A and B,

$$\bar{p}_A = p_A x_A \tag{XII.53}$$

$$\bar{p}_B = p_B x_B \tag{XII.54}$$

$$\bar{p}_C = p_C(1 - x_A - x_B) \tag{XII.55}$$

$$p = p_A x_A + p_B x_B + p_C(1 - x_A - x_B) \tag{XII.56}$$

$$y_A = \frac{\bar{p}_A}{p} \tag{XII.57}$$

$$y_B = \frac{\bar{p}_B}{p} \tag{XII.58}$$

$$1 - y_A - y_B = \frac{\bar{p}_C}{p} \tag{XII.59}$$

From these equations we can readily derive

$$y_A = \frac{\alpha_{AC} x_A}{1 + (\alpha_{AC} - 1)x_A + (\alpha_{BC} - 1)x_B} \tag{XII.60}$$

$$y_B = \frac{\alpha_{BC} x_B}{1 + (\alpha_{AC} - 1)x_A + (\alpha_{BC} - 1)x_B} \tag{XII.61}$$

where

$$\alpha_{AC} = \frac{p_A}{p_C}$$

$$\alpha_{BC} = \frac{p_B}{p_C}$$

These equations can also be used as good approximations for the case of constant pressure since the ratios of the vapor pressures of the pure components do not change much over the relatively narrow temperature ranges encountered in distillation.

The treatment of nonideal ternary systems is beyond the scope of this test.   For one particular case, that of the ternary oxygen–nitrogen–argon, reference may be made to a paper by Hausen.[1]   For a more thorough treatment of ternary systems both from the mathematical and the graphical standpoint, reference may be made to the book by J. P. Kuenen (*op. cit.*).

N-COMPONENT SYSTEMS

Graphical methods are out of the question for such complex systems, and one must have recourse to purely algebraic relations.   In the general

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[1] HAUSEN, H., *Forschung Gebiete Ingenieur.*, **6B**, 9–22 (1935).

case there would be relationships of the form

$$y_i = \phi(p,t,x_A,x_B, \cdots ,x_{N-1}) \tag{XII.62}$$

Since there are N degrees of freedom (assuming two phases) all but one of these variables are independent. Furthermore, the function would depend on the nature of the components present. Unless some simplifying assumptions can be made, the situation is hopelessly complex as far as any useful algebraic treatment is concerned.

Ideal Solution, Vapor Phase an Ideal Gas.—If one can assume that the liquid phase is an ideal solution, then Eq. (XII.62) can be greatly simplified to

$$y_i = \phi(p,t,x_i) \tag{XII.63}$$

In other words, the concentration of a given component in the vapor now depends only on *its* concentration in the liquid (p and t fixed); it is not affected by the concentrations or the identity of all the other components in the liquid. For example, a 10 mole per cent concentration of benzene in an ideal solution will give a certain concentration of benzene in the vapor *at a given p and t* regardless of what the other components are or of their relative amounts. If, however, only the pressure *or* the temperature is known, the nature and relative amounts of the other components will enter into the calculation, as will be illustrated presently (page 578). For the special case where, in addition to an ideal-liquid solution, the vapor can be considered an ideal gas, $\phi(p,t,x_i)$ has a quite simple form. Thus from relations previously developed, we have

$$\bar{p}_i = p_i x_i \tag{XII.64}$$
$$y_i p = p_i x_i \tag{XII.65}$$
$$p = \Sigma p_i x_i \tag{XII.66}$$
$$y_i = \frac{p_i x_i}{\Sigma p_i x_i} \tag{XII.67}$$

Dividing numerator and denominator of the right-hand side of Eq. (XII.67) by p_B,

$$y_i = \frac{\alpha_{iB} x_i}{\alpha_{AB} x_A + x_B + \alpha_{CB} x_C + \cdots + \alpha_{NB} x_N} = \frac{\alpha_{iB} x_i}{\Sigma \alpha_{iB} x_i} \tag{XII.68}$$

The relative volatilities α are in this case referred to component B, but, of course, any one of the components can be chosen. (Note that $\alpha_{BB} = 1$.) By exactly analogous methods one can derive

$$x_i = \frac{y_i/\alpha_{iB}}{\Sigma(y_i/\alpha_{iB})} \tag{XII.69}$$

As in the binary case, these equations are strictly for constant temperature; but since the relative volatilities change very slowly with temperature, they can also be used for the case of constant pressure with

satisfactory accuracy for distillation calculations. In using Eqs. (XII.68) or (XII.69) for the case of constant pressure it is necessary to know the temperature to evaluate the α's, but only an approximate value is necessary. A trial value of the temperature can always be checked by the relation

$$\Sigma p_i x_i = p \qquad (XII.70)$$

Illustration 6.—An ideal liquid solution at 100°C. and 2-atm. pressure contains 20 mole per cent toluene. What will be the concentration of toluene in the vapor in equilibrium with this solution? The vapor pressure of toluene at 100°C. is 557 mm.

Using Eq. (XII.65), $y_T = \dfrac{0.20 \times 559}{2 \times 760} = 0.0735$

Note that we obtain this figure without any knowledge about the other components in the solution. They could not, however, be chosen arbitrarily because only certain systems would give the pressure and temperature stated.

If only the pressure or the temperature is given, then the complete composition of the liquid phase must be known, as is shown in the following.

Illustration 7.—Calculate (1) the composition of the vapor in equilibrium at atmospheric pressure with a liquid whose composition is 10 per cent n-hexane, 30 per cent benzene, 40 per cent n-heptane, and 20 per cent n-octane (all mole per cents); (2) the equilibrium temperature. Assume ideal solution and ideal gases and that the vapor pressures of the pure components as a function of temperature can be represented by the equation $\log p_{mm} = A - B/T°K$. with the following values of the constants:[1]

	A	B
Hexane (component A).............	7.7215	1,654.6
Benzene (component B).............	7.6559	1,686.8
Heptane (component C).............	7.5917	1,750.0
Octane (component D).............	7.7503	1,941.4

The normal boiling points range from about 69 to 126°C. For trial, take $t = 100$°C.

The following values of α referred to benzene are then calculated from the vapor-pressure equations

Substance	Vapor pressure, mm.	Relative volatility
Hexane.................................	1,935	$\alpha_{AB} = 1.418$
Benzene................................	1,364	$\alpha_{BB} = 1.000$
Heptane................................	798	$\alpha_{CB} = 0.585$
Octane.................................	352	$\alpha_{DB} = 0.258$

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[1] BEATTY and CALINGAERT, *loc. cit.*

Substituting in Eq. (XII.68),

$$y_A = \frac{1.418 \times 0.100}{1.418 \times 0.100 + 0.300 + 0.585 \times 0.400 + 0.258 \times 0.200} = 0.195$$

$$y_B = 0.412$$
$$y_C = 0.322$$
$$y_D = 0.071$$
$$\Sigma p_i x_i = 1{,}935 \times 0.100 + 1{,}364 \times 0.300 + 798 \times 0.400 + 352 \times 0.200 = 993$$

∴ by Eq. (XII.70) the trial temperature is too high. The results of a few more trials are as follows:

t, °C.	Vapor pressures				$\Sigma p_i x_i$
	A	B	C	D	
90	1,462	1,023	592	253	741
95	1,690	1,186	689	299	860

From a plot of $\Sigma p_i x_i$ vs. t, the temperature for $\Sigma p_i x_i = 760$ is found to be 90.9°C. At this temperature the values of α are as follows:

$$\alpha_{AB} = 1.425$$
$$\alpha_{BB} = 1.000$$
$$\alpha_{CB} = 0.577$$
$$\alpha_{DB} = 0.247$$

With these corrected values of α, the vapor composition is then found to be

$$y_A = 0.197$$
$$y_B = 0.415$$
$$y_C = 0.320$$
$$y_D = 0.068$$

The differences between these values and those calculated on the basis of the trial temperature of 100°C. are well within the errors that are involved in the basic assumptions, and hence we may conclude that only a very approximate temperature is necessary for the calculation of vapor compositions.

Nonideal Gas. The Equilibrium Ratio K.—If the vapor cannot be considered an ideal gas, one of the commonest methods of procedure is to write Eq. (XII.63) in the form

$$y_i = K_i x_i \qquad \text{(XII.71)}$$

where, in general, K_i is a function of p, t and the nature and composition of the solution. K has generally been referred to as an "equilibrium constant," but "equilibrium ratio" would be a better term since it is not in any sense a constant. K is commonly assumed to be independent of the composition, which is tantamount to the assumption that the liquid phase is an ideal solution. This introduces a tremendous simplification, as we have already shown.

If the vapor is an ideal gas, it follows from Eq. (XII.65) that

$$K = \frac{p_i}{p} \qquad (XII.72)$$

By analogy to this equation, Lewis and Luke[1] write, for the case where the vapor is not an ideal gas,

$$K = \frac{f_{p_i}}{f_p} \qquad (XII.73)$$

where f_{p_i} is the fugacity of pure component i at the given temperature and at the vapor pressure of the pure component and f_p is the fugacity of pure i in the gaseous state at the temperature and total pressure of the solution.

Souders, Selheimer, and Brown[2] write this equation in slightly different form, $viz.$,

$$K = \frac{f_L}{f_V} \qquad (XII.74)$$

where f_V is the same as f_p but f_L is the fugacity of the pure component as a liquid at the pressure and temperature of the solution. From the equation for the change of fugacity with pressure (III.144) combined with the assumption that the volume of the liquid is independent of the pressure, one readily obtains

$$\frac{f_{p_i}}{f_L} = e^{\frac{v_i}{RT}(p_i - p)} \qquad (XII.75)$$

This ratio is not far from 1.00 as long as the pressure is less than 100 atm., and hence Eqs. (XII.73) and (XII.74) are substantially equivalent.

Both of these equations should be regarded as empirical equations without a strictly rational basis. An attempt at a rational derivation[3] can be made on the basis of the general equations for a binary system derived in Chap. IV, and this appears desirable in order to make clear some of the limitations of these equations. From Chap. IV,

$$\frac{y}{x} = \frac{e^{\left[\frac{1}{RT}\int \bar{v}_A{}' dp\right]}}{e^{\left[\frac{1}{RT}\int \bar{v}_A{}'' dp\right]}} \qquad (IV.143)$$

This is a general equation for two-phase equilibrium in a binary system. If we assume that both the liquid and vapor phases are ideal solutions, $\bar{v}_A'$ and $\bar{v}_A''$ are independent of composition and functions of p and t only.

[1] LEWIS, W. K., and C. D. LUKE, *Trans. A. S. M. E.*, **54**, 55 (1932).

[2] SOUDERS, M., JR., C. W. SELHEIMER and G. G. BROWN, *Ind. Eng. Chem.*, **24**, 517 (1932).

[3] DODGE, B. F., and R. H. NEWTON, *Ind. Eng. Chem.*, **29**, 718 (1937).

Let us further assume that component A can exist in the pure state either as a liquid or as a vapor at the p and t of the solution. (This is, of course, impossible for stable equilibrium. In any ideal binary solution, the more volatile component can exist pure only as a vapor and the less volatile component only as a liquid at the p and t of the solution.) Then we can write

$$\bar{v}'_A = v'_A$$
$$\bar{v}''_A = v''_A$$

and since

$$\frac{1}{RT} \int v_A \, dp$$

is, by definition, the natural logarithm of the fugacity of component A, Eq. (IV.143) becomes

$$\frac{y}{x} = \frac{f_L}{f_V} = K$$

This derivation was only for a binary solution, but it seems reasonable to extend it to apply to any ideal solution since in such a solution it makes no difference whether the environment of any given component is one other single component or a complex mixture.

As a result of this brief discussion it should be clear why Eq. (XII.74) is an empirical relation that should be used with a full knowledge of its limitations. It has been widely applied, and conclusions based on it have at times been drawn without due regard to these limitations. On the other hand, it offers the only practicable means available at the present time for equilibrium calculations in the case where the vapor is not an ideal gas. It may at least be expected to yield more accurate results than the ideal-gas law in dealing with systems under elevated pressures.

In considering the numerical value of K, it is useful to bear in mind that at two points the value of K is definitely fixed and known in advance for any component. Thus K is unity at the vapor pressure of the pure component for the temperature in question, and it is again unity at the critical point of the given mixture. These two facts are useful guides in considering trends in K values.

Calculation of K.—The equilibrium ratio K is readily obtained from experimental data; but such data are as yet very meager, and it has generally been necessary to calculate K from the data on pure hydrocarbons or on a selected few binary solutions by means of equations such as Eq. (XII.73) or (XII.74). Values obtained in this way have been extensively applied in calculations on various unit operations involving petroleum hydrocarbons, and such values for several common hydrocarbons may be obtained from a number of sources.[1] Because of the

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[1] SOUDERS, SELHEIMER, and BROWN, *op. cit.* LEWIS, W. K., and W. C. KAY, *Oil Gas J.*, **32**, No. 45, 40 and 114 (1934). SHERWOOD, T. K., "Absorption and Extrac-

widespread use of these data, it seems desirable to examine more closely the methods by which they have been obtained.

Values have been obtained in two different ways, both of which involve some doubtful extrapolations into unstable regions. Consider, for example, the method of Lewis and Kay, which is based on Eq. (XII.73). For any pure hydrocarbon, f_p, has no real physical meaning when the temperature in question is above the critical temperature because the substance can obviously have no real vapor pressure. For example, methane at 70°F. is in this category. Likewise, f_p has no real significance when the temperature is below critical and the pressure above the vapor
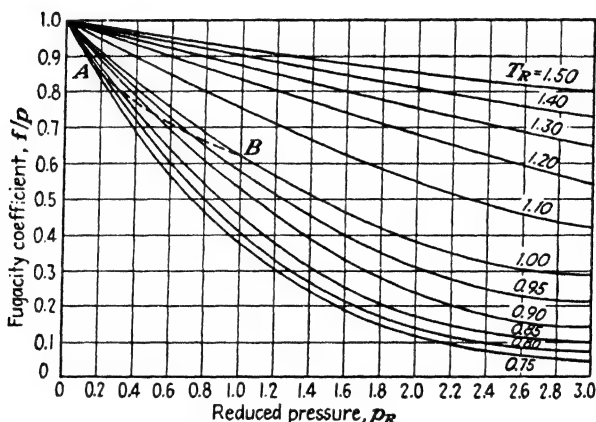
Fig. XII.39.—Fugacity coefficient of pure hydrocarbons. [*Reproduced from a paper of Lewis and Kay, Oil and Gas Journal,* **32**, 114 (1934).]

pressure, because the component cannot exist as a gas under these conditions. Butane at 100°F. and 20 atm. would be a case in point.

Lewis and Kay obtain the fugacities for use in Eq. (XII.73) from a generalized chart of fugacity coefficient[1] (ratio of fugacity to pressure) vs. reduced pressure with parameters of reduced temperature. Their chart is reproduced in Fig. XII.39. Line AB is the phase boundary line, *i.e.*, it connects the reduced vapor pressure with the reduced temperature. In the region above AB and above $T_R = 1.00$, the pure hydrocarbons are stable as gases and the fugacity is readily calculated from *pvt* data by the methods outlined in Chap. VI. The chart in this region is substantially identical with Fig. VI.12, which is a generalized

tion," McGraw-Hill Book Company, Inc., New York, 1937. BROWN, G. G., and M. SOUDERS, Section in "The Science of Petroleum," pp. 1544–1579, Oxford University Press, New York, 1938.

[1] This term has been used interchangeably with the term "activity coefficient" to designate this ratio.

fugacity-coefficient chart for all substances. In the region below AB and $T_R = 1.00$, the pure hydrocarbons are stable only as liquids, but the chart is actually used in this region to obtain f_p, the fugacity of the hydrocarbon as a gas. Therefore, instead of plotting the fugacity coefficient of the liquid hydrocarbon, it seemed more logical to calculate values of f_p from Eq. (XII.73) in the form

$$f_p = f_{p_i} \frac{x}{y}$$

utilizing some of the available data on solutions, and this was the method employed to obtain the curves of Fig. XII.39 in this region. It amounts to an extrapolation of the curves in the gaseous region into the liquid region where gases are not stable, using the data on solutions to guide the extrapolation. Thus x and y are given by the experimental data,[1] f_{p_i} is readily obtained from line AB for hydrocarbons whose critical temperatures are above the given temperature. In the case of hydrocarbons whose critical temperatures are below the given temperature, for example, CH_4 at room temperature, some means of extrapolating AB into the unstable region is necessary. It has been suggested that Eq. (XII.73) might be used for the extrapolation, and Lewis and Kay tried this for methane, using the methane-propane solution data. They concluded that it was a satisfactory approximation for moderate pressures and for temperatures not too far above critical. Another method of extrapolation is by a linear plot of log p_i or log f_{p_i} vs. $1/T$.

The calculation of K will be illustrated by a few examples.

Illustration 8.—Calculate K for n-butane at 100°F. and 25 atm., using the method of Lewis and Kay.

From Table IV in the Appendix,   Critical temperature $= 426°K$.
                                Critical pressure $= 36.0$ atm.

$$T_R = \frac{460 + 100}{426 \times 1.8} = 0.730$$

$$p_R = \tfrac{25}{36} = 0.695$$

From Fig. XII.39, $f_p/p = 0.50$, and $f_p = 0.50 \times 25 = 12.5$.
The vapor pressure of butane at 100°F.[*] is 3.5 atm.

$$p_R = \frac{3.5}{36} = 0.097$$

From Fig. XII.39, $\dfrac{f_{p_i}}{p} = 0.90$

Then $f_{p_i} = 3.2$

[1] Methane-propane data of Sage, Lacey, and Schaafsma [*Ind. Eng. Chem.*, **26**, 214 (1934)]. *N*-pentane–*n*-heptane, Cummings, Stone, and Volante [*Ind. Eng. Chem.*, **25**, 728 (1932)].

[*] Copson, R. L., and P. K. Frolich, *Ind. Eng. Chem.*, **21**, 1116 (1929).

f_{p_i} could also be read directly from the graph of the fugacities of liquid hydrocarbons at their vapor pressure against the temperature, given in the book by Sherwood* and attributed to W. C. Kay.

Finally,
$$K = \frac{f_{p_i}}{f_p} = \frac{3.2}{12.5} = 0.26$$

Illustration 9.—Calculate K for methane at 100°F. and 25 atm.

This differs from the butane case in the fact that the temperature is well above the critical temperature of methane, and hence a considerable extrapolation of the vapor-pressure curve above the critical point is necessary to evaluate f_{p_i}.

From Table IV in the Appendix,   Critical temperature = 190.6°K.
Critical pressure = 45.8 atm.
$$T_R = 1.63, \qquad p_R = 0.545$$
$$\frac{f_p}{p} \text{ (from Fig. XII.39)} = 0.98$$
$$f_p = 24.5$$

To get f_{p_i}, the vapor pressure of CH_4 might be extrapolated on a log p vs. $1/T$ graph; or, as Sherwood suggests, log f_{p_i} can be plotted against $1/T_R$, yielding a straight line that can be extrapolated above the critical point. Using the latter procedure,

$$f_{p_i} = 190$$
Then,
$$K = \frac{190}{24.5} = 7.8$$

The method employed by Brown and coworkers to calculate K differs materially from that just described. At temperatures below critical the fugacity of the vapor at the vapor pressure is calculated by methods already described or is obtained from a fugacity-coefficient chart. This value will also be that of the liquid at the vapor pressure, and from this the fugacity of the liquid at some other pressure is obtained from an integration of the equation for change of f with pressure, the volume being assumed constant. This procedure gives f_L of Eq. (XII.74). f_V is calculated by the usual methods for a gas as long as the pressure is less than the vapor pressure. These calculations gave K for the lower saturated hydrocarbons up to and including pentane for $T_R = 0.9$ and 1.0 and up to pressures of about 500 lb. per sq. in. All these values of K are greater than unity since by the above method K can be calculated only when the pressure is equal to or less than the vapor pressure. At the vapor pressure, $K = 1$ in all cases; for all pressures less than the vapor pressure, $K > 1$. Values of $K < 1$ are obtained by extrapolation on a log K vs. log p plot, using the curves for $T_R = 0.9$ and 1.0 as a guide since these cover practically the whole pressure range [see Fig. 1 in *Ind. Eng. Chem.*, **24**, 517 (1932)].

At temperatures above critical, f_V is readily obtained by orthodox methods, but f_L is the fugacity of a liquid at a temperature above critical

* *Loc. cit.*

where liquid cannot exist. The method used by Brown and coworkers to get K in this region is as follows: K values were read from the log K vs. log p plot just referred to along isobars and plotted as log K vs. T_R. Extrapolation above $T_R = 1.0$ was guided by scattered data on heats of solution, which permitted a calculation of the slopes by means of Eq. (IV.207) and by some experimental measurements of K. In other words,
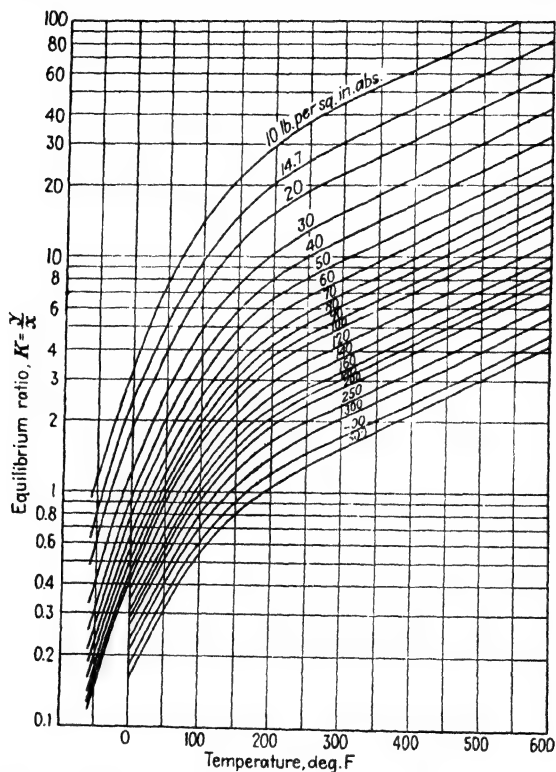
Fɪɢ. XI..40.—Equilibrium ratio K for propane. Critical temperature is 205°F.; critical pressure is 630 lb. per sq. in. (*Reproduced from G. G. Brown and M. Souders, Jr., "Science of Petroleum," Fig. 4, p. 1547, Oxford University Press, New York, 1938.*)

in this region K is based on solution data rather than on data for pure compounds as was the case for the region below $T_R = 1.0$.

These procedures have obvious flaws but are the best available at the present time. It was felt to be desirable to give this brief outline of them in order that the user of K data should appreciate the uncertainties involved and not base unwarranted conclusions on them.

Let us briefly summarize the uncertainties in the calculation of K from Eq. (XII.74) in the following way:

1. For all values of $K > 1$, the pressure is either less than the vapor pressure at the given temperature or the temperature is above critical. In either case, no liquid phase for the pure component is thermodynamically possible, and hence f_L is empirical.

2. For all values of $K < 1$, either the pressure is greater than the vapor pressure and no stable vapor phase of the pure component is possible, or the temperature is above critical and no liquid phase is possible. Therefore, either f_V or f_L is empirical.

Use of K Charts.—Charts of K vs. temperature with pressure parameters covering a wide range of conditions for the lower saturated hydrocarbons up to and including n-heptane are given by Brown and Souders.[1] Their chart for propane is reproduced in Fig. XII.40. These charts give calculated values of K and should be used with a full realization of their limitations as previously discussed. It will be found that other charts may give values differing considerably from these, especially for methane and ethane.

The use of K values to calculate the composition of either phase in a liquid-vapor equilibrium, given the composition of the other, is illustrated by the following numerical example.

Illustration 10.—Calculate the pressure and composition of the vapor in equilibrium with a liquid containing 5 per cent CH_4, 10 per cent C_2H_6, 30 per cent C_3H_8, 25 per cent iso-C_4H_{10}, and 30 per cent n-C_4H_{10} (mole per cents) that is at 100°F.

Values of K will be taken from the charts of Brown and Souders.[2] Since K is a function of both p and t and p is unknown, a trial solution is necessary. The criterion for correct pressure is

$$\Sigma y = \Sigma Kx = 1$$

We can also write
$$y_i = \frac{K_i x_i}{\Sigma Kx}$$

The advantage of this form of the equation for y is that it involves only ratios of K, and these do not change rapidly with either p or t. Consequently, if one wishes to calculate only the vapor composition, just an approximate value of either p or t is required.

Trial 1.—$p = 150$ lb. per sq. in. abs.

Hydrocarbon	K	Kx	$\dfrac{Kx}{\Sigma Kx} = y$
C_1	8.5	0.425	0.320
C_2	2.9	0.290	0.219
C_3	1.15	0.345	0.260
iso-C_4	0.57	0.143	0.108
n-C_4	0.41	0.123	0.093

$$\Sigma Kx = 1.326$$

[1] *Loc. cit.*
[2] *Op. cit.*

Trial 2.—p = 300 lb. per sq. in. abs.

C₁	5.1	0.255	0.316
C_1	5.1	0.255	0.316
C_2	1.66	0.166	0.206
C_3	0.72	0.216	0.267
iso-C_4	0.36	0.090	0.111
n-C_4	0.27	0.081	0.100

$$\Sigma K x = 0.808$$

The differences between the vapor compositions for these two trials is scarcely significant, and we can safely assume that any trial which gives a $\Sigma K x$ within 20 per cent of unity is satisfactory. Of course, to obtain the pressure further trials are necessary, but these can be reduced to a minimum by plotting $\Sigma K x$ vs. p. In this way we find that, when $\Sigma K x = 1$, $p = 220$ lb. per sq. in. abs.

The method is just the same when the temperature is the unknown, the pressure having been specified.

When equilibrium liquid composition is to be calculated from vapor composition, the procedure is the same except that the equations employed are

$$x = \frac{y}{K} \qquad\qquad (XII.76)$$

and

$$x = \frac{y/K}{\Sigma(y/K)} \qquad\qquad (XII.77)$$

Experimental Equilibrium Ratios.—All the values of K that we have used were calculated ones based on certain assumptions and extrapolations, with a few scattered experimental points acting as a rough guide. Experimental data in this field are very fragmentary, but a good beginning has been made in the case of petroleum hydrocarbons by several investigators. Sage and Lacey[1] have completely summarized the available information on equilibrium ratios for methane in several hydrocarbon systems. In Fig. XII.41, reproduced from their paper, is shown the effect of pressure and temperature on K for both methane and propane in the binary system methane-propane. Note that $K = 1.0$ at the critical point of the system and again at the vapor pressure of propane for the given temperature. For example, the curve for propane at 70°F. starts at $K = 1$ and $p = 75$ (approximately), the vapor pressure of propane. K decreases as the pressure increases, and then K increases, reaching the value 1.0 again at about 1,400 lb. per sq. in., the critical pressure of the methane-propane system at this temperature. The continuation of the curve above the $K = 1$ abscissa gives the values of K for methane. The agreement of the values in Fig. XII.41 with the calculated ones of Brown and Souders is quite good for propane, but there is considerable disagreement in the case of methane.

[1] SAGE, B. H., and W. N. LACEY, *Ind. Eng. Chem.*, **30**, 1296 (1938).

All the calculated values of K are based on the assumption of ideal solutions, and some of the data presented by Sage and Lacey permit us to make a check on this assumption.   In the following tabulation values
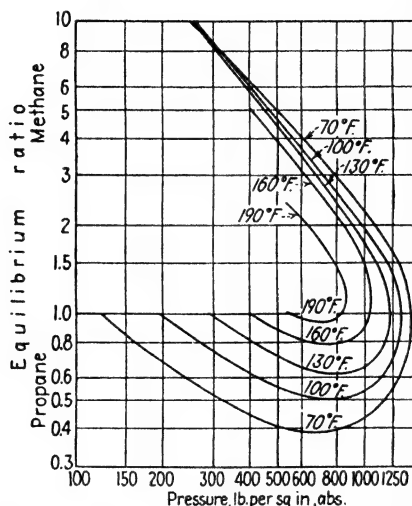
Fig. XII.41.—Equilibrium ratios for methane and propane in the system methane-propane.
[*Reproduced from Sage and Lacey, Ind. Eng. Chem.,* **30**, 1299, *Fig.* 3 (1938).]

are given for the equilibrium ratio of methane in several systems, at 160°F. and 500 lb. per sq. in.

System	K
Methane–propane.............	3.89
Methane–n-pentane...........	6.30
Methane–n-hexane............	7.08
Methane–cyclohexane..........	9.63
Methane–nitrogen–heptane......	6.86
Methane–nitrogen–toluene......	12.4
Methane–nitrogen–benzene......	14.6 (at 130°F. For 160°F. the value would
Methane–crystal oil	6.7 be greater.)

If these solutions were ideal, the K values should be identical but there are considerable differences even in the case of systems containing only saturated paraffin hydrocarbons.   On the other hand, it is likely that methane is an extreme case, and for higher hydrocarbons the agreement would be better.   In any case, it is apparent that K is a function not only of p and t but also of the nature and amount of the other components. Sage and Lacey present a tentative correlation of K for methane with the molecular weight and chemical nature of the other components present.   The correlation was tested with satisfactory results on a

methane–crude oil system but with rather poor results when it was applied to the system methane–n-butane.

Sage, Hicks, and Lacey[1] have presented tentative correlations for K values of several light hydrocarbons, up to and including heptane.

Brown and Souders also considered deviations from the ideal-solution law and show that deviations are greatest for the low-molecular-weight hydrocarbons and when the particular component is present in relatively small proportion. They also give a graph of correction factors for varying concentration in the liquid and for different hydrocarbons.

Kay[2] compared his measurements on the system ethane–n-heptane with values of K given by Sherwood and found fair agreement as long as the critical region was not approached.

Further evidence of the effect of the nature of the solution on the values of K is offered by Sage and Lacey[3] in a recent paper. Data on the ternary system methane–propane–n-pentane, at 100°F., show considerable variations of K for all three components at 500, 1,000, and 1,500 lb. per sq. in. as the solution changed progressively from one containing no propane to one containing no pentane. For example, at 1,000 lb. per sq. in. the K for pentane varied from 0.08 to 0.50. The percentage change was less for propane and methane. This effect is considerably less pronounced at lower pressures.

[1] SAGE, B. H., B. L. HICKS, and W. N. LACEY, Preprint of paper presented at eighth midyear meeting of A.P.I., May 24, 1938.

[2] *Loc. cit.*

[3] SAGE, B. H., and W. N. LACEY, Preprint of paper presented at twenty-second annual meeting of A.P.I., Nov. 7, 1941.

CHAPTER XIII

DISTILLATION PROCESSES

GENERAL PRINCIPLES

The possibility of separating solutions of volatile substances by the various processes included under the general head of distillation depends on two fundamental factors, (1) a difference in the compositions of a liquid and a vapor phase at equilibrium and (2) a difference in density of the two phases. All the operations used in distillation processes involve first a contact between phases to bring about certain changes in composition, followed by a physical separation of the phases, usually by gravity. The second factor involves no thermodynamical considerations and will be dismissed without further discussion, whereas the first factor was considered in some detail in the preceding chapter. In the present chapter we are to consider several important processes in which these two factors are applied in a variety of ways.

Fig. XIII.1.—Elementary processes of vaporization and condensation.

Let us first review some of the general principles of the two fundamental operations of vaporization and condensation which are involved in all distillation processes.

Integral Vaporization and Condensation.—In the temperature-composition diagram for one type of binary system shown in Fig. XIII.1, point A represents a mixture of composition x_1 that is entirely liquid. As this liquid is heated at constant pressure, it follows the path AB (constant composition). At point J the first trace of vapor is produced (bubble point), and this vapor has the composition y_1, corresponding to point D. (Note that the coexisting phases at equilibrium must lie along isotherms.) As the heating is continued at constant composition and if no material is removed from the system, a point such as E is reached where the system is a heterogeneous mixture of the two phases of the compositions indicated by F and G. As one continues to add heat to the

590

system, always at constant pressure and constant total composition, point H is reached where there is only a trace of liquid remaining (dew point); this liquid has the composition represented by point C. Above H is the region of superheated vapor. When the vaporization process is stopped before the state of the system reaches that corresponding to H, the process is one of partial vaporization since there is still some residual unvaporized liquid. When it is carried to the state H or beyond, it is referred to as "total vaporization."

A process of vaporization such as is represented by the path JE in which all the vapor generated is allowed to remain in contact with all the residual liquid is commonly called "flash distillation." It will also be referred to as "integral vaporization" to distinguish it from "differential vaporization," to be discussed later (page 592). The net result of the process has been the separation of the original liquid of composition x_1 into two fractions, one poorer in component A (composition x_2) and one richer (y_2).

A condensation process the exact reverse of the vaporization one just described may be carried out as follows: Starting at point B, a superheated vapor mixture of composition x_1 is cooled at constant pressure, and at H a trace of liquid appears. As cooling is continued, the amount of liquid steadily increases until at J only a bubble of vapor remains and we have saturated liquid. Further cooling to A gives "subcooled" liquid. When the state of the system lies between points H and J, the cooling step would be known as "partial condensation" since some vapor remains uncondensed. Cooling to J or to still lower temperatures gives "total condensation." Obviously, it is only by partial, as distinct from total, condensation that any separation of the components can be produced.

The process of partial condensation just illustrated, in which all the condensate produced remains in contact with the residual vapor and is presumed to be in phase equilibrium with it, will be known as "integral condensation" by analogy with the corresponding vaporization process. The maximum possible enrichment of the vapor in the more volatile component which can be obtained by such a process is, for this particular case, that corresponding to composition y_1.

A combination of these two processes of vaporization and condensation will lead to an improvement in the degree of separation of the liquid of composition x_1 over that possible with either process alone. Suppose the liquid is vaporized until state E is reached and then the vapor mechanically separated from the liquid and partially condensed to state L. There will then be a residual vapor represented at D and a residual liquid (J) of the same composition as the original liquid. Therefore, the net result of this process is the separation of a liquid of composition x_1 into

two fractions one (state M) of composition y_1 (this would, of course, be an x or composition of liquid, after total condensation) and the other (state F) of composition x_2. By continuing this process on the two liquids represented by F and M and making suitable combinations of residues, which are in turn subjected to similar processes, it is possible completely to separate solution A into its two pure components. Such a process is very laborious and never used in practice since the same result can be accomplished in a much simpler way, but the same principles are involved in all practical processes.

Differential Vaporization and Condensation.—Vaporization of a liquid can also be carried out in the following way, which will be illustrated by reference to Fig. XIII.1. Liquid at state J is vaporized, and the first small increment of vapor (state D) is at once removed from contact with the liquid and totally condensed. The residual liquid in the still is now slightly less rich in the more volatile component, and hence its composition is represented on the liquid line just a little to the left of J. If the vaporization is continued, with each differential increment of vapor being removed and condensed as it forms so that the residual liquid at any time is in equilibrium only with the last increment of vapor, the state of the unvaporized liquid will move continuously along the liquid line, and increments of vapor will be represented by corresponding points along the vapor line. This process will be known as "differential distillation";[1] with it one can obtain a small amount (strictly speaking, only a differential amount) of the pure, less volatile component but no portion of the more volatile component in the pure state. In this process it is assumed that there is no partial condensation which would cause any of the vaporized material to be sent back to the still as a reflux liquid.

The exact reverse of this process, *viz.*, the condensation and continuous removal from contact with the vapor of small (infinitesmal at the limit) increments of liquid, will be called "differential condensation." Starting with a vapor in state G, differential condensation can, when carried to the limit, yield a small amount of the pure, more volatile component, but the greatest enrichment in the less volatile component is that corresponding to point F.

By a combination of these two processes in such a way that the liquid condensate is continuously returned as a reflux to the still, it is theoretically possible to effect a complete separation of the liquid of composition x_1 into the two pure components. Such a process would be very uneconomical because of the great heat consumption since the heat added for vaporization is all dissipated in the condensation and the condensate must be continually reboiled.

[1] The term in common usage for this process is "simple distillation." but it is believed that the one gives above is preferable.

Rectification.—The distillation process most widely used in practice for the separation of volatile liquids is that of rectification, in which a stream of vapor is brought into continuous countercurrent contact with a stream of liquid in a suitable contacting apparatus known as a "rectifying column." Figure XIII.2 represents diagrammatically a simple rectifying column. A liquid stream L_1 produced from the vapor V_1 by a condenser enters the top of the column, a vapor stream V_2 produced in a boiler below the column enters at the bottom, and the two flow countercurrently in contact. The methods of producing the streams and of bringing about intimate contact between phases may vary, but they are immaterial as far as the fundamental principle of separation by rectification is concerned. Consider any level in the column as shown, and let vapor V and liquid L have compositions represented by points H and F, respectively, in Fig. XIII.1. Vapor H is not in equilibrium with liquid F with which it is in contact; the equilibrium liquid would be that at C. Consequently, there is a difference in chemical potential, and a mass transfer will occur between the vapor and the liquid, with the result that the vapor composition tends to move toward point G and the liquid toward C. In other words, the vapor becomes enriched in the more volatile component and the liquid impoverished in the same component. Furthermore, it is to be noted that the mass transfer is two-way: it involves both condensation and vaporization. In other words, instead of having these two processes occurring separately in different parts of the apparatus as in fractional distillation, in rectification they are occurring simultaneously, with a resultant great saving in heat consumption.
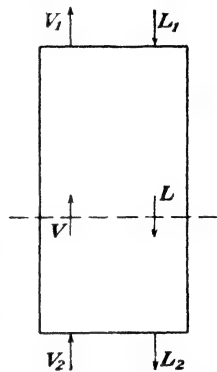
Fig. XIII.2.—Principles of rectification.

The same transfer process occurs at all levels in the column, with the result that the ascending vapor becomes steadily richer in the more volatile component and the descending liquid poorer in the same component. By adding a condenser at the top of the column, the vapor V_1 is condensed, part of it withdrawn as the overhead product, and part of it returned to the column as the reflux liquid L_1. The liquid L_2 leaving the bottom of the column goes to a boiler or still, where part of it is vaporized to form the vapor V_2 and the rest is drawn off as the bottom product. To make a continuous separation of a binary solution, it is generally fed as a liquid at some intermediate level in the column and the two products withdrawn at the top and bottom, respectively.

Separation of Azeotropes.—All processes for separation of solutions by distillation depend on a difference in composition between the two phases

that coexist at equilibrium. When the equilibrium relationship is one that exhibits a maximum or a minimum in the boiling-point curve, then, as was shown in the previous chapter, the two phases become identical in composition at this point and no further separation is possible. In Fig. XIII.3, which gives the temperature-composition diagram for a solution with a minimum boiling point, x_A is the composition of the azeotrope, which behaves just like a pure liquid in any distillation process. A solution of composition x_1 could be separated into pure B and the azeotrope, but it would be impossible in an ordinary distillation process to make any pure A. Similarly, starting with a solution of composition x_2, one could separate into azeotrope and pure A but not pure B. Since the azeotrope behaves like a pure component, a tx diagram like that in

Fig. XIII.3 may be regarded as consisting of two diagrams of the ordinary type separated by the ordinate at x_A.

Details of methods for the separation of azeotropic mixtures are beyond the scope of this work, but it may be stated in passing that there are two general ways in which it may be accomplished by distillation: (1) by altering the distillation pressure and thereby changing the composition of the azeotrope (see Chap. XII, page 544); (2) by adding a third (and sometimes also a fourth) component and thus changing the thermodynamic environment so that the vapor-pressure relations are modified and separation becomes possible. The latter method is the one commonly used for the production of absolute alcohol. Addition of benzene to the constant-boiling mixture of ethyl alcohol and water yields a ternary constant-boiling mixture (heterogeneous) boiling at 64.9°C. at 1 atm. that can be taken off as head product in a rectifying column, leaving absolute alcohol as the bottom product. The benzene is recovered from the distillate by dilution and mechanical separation, and the resulting dilute alcohol is reconcentrated to the constant-boiling mixture in another column.[1]

Azeotropic Distillation.—The process for separating an azeotrope by adding another component which forms a heterogeneous constant-boiling mixture as in the case just discussed is commonly called "azeotropic distillation," though this is a misnomer to those who restrict the term "azeotrope" to a homogeneous constant-boiling mixture. A similar

Fig. XIII.3.—Separation of solutions with a minimum boiling point.

[1] For further details see the following papers: COOLEY, L. C., *Chem. Met. Eng.*, **34**, 725 (1927). GUINOT, H., and F. W. CLARK, *Trans. Inst. Chem. Eng.*, **16**, 189 (1938).

process (in principle) has come into prominence in recent years for the separation of acetic acid–water solutions, and the same principle is applicable to other cases. Acetic acid and water do not form an azeotropic mixture, but the separation is difficult owing to the small difference between the compositions of the coexisting phases. By adding a third component that is practically immiscible with water, the head product of the column is not water but the heterogeneous constant-boiling mixture of water and the added component, or so-called "entrainer." This boils at a lower temperature than water, and hence the effect is to increase very materially the terminal temperature difference in the system. For example, if the entrainer were isopropyl ether, the boiling point of the heterogeneous mixture with water is 61°C. and the column is called upon to make a separation between head and bottom products boiling at 61 and 118°C. (acetic acid), respectively, instead of at 100 and 118°C. The head-product mixture is separated mechanically and the entrainer returned to the column. (Note the similarity between this process and a steam distillation.) Further details on the process may be obtained by reference to a paper by Othmer.[1]

MINIMUM WORK OF SEPARATION

To carry out the separation of a solution by distillation or by any other process requires the expenditure of a certain amount of energy in the form of either heat or work. In the great majority of distillation processes, heat rather than work is used, but there are a few cases, *viz.*, the low-temperature separation of gases and the vapor-recompression processes, where work is done to carry out a distillation. In either case, it is desirable from an economic standpoint to use as small an amount of heat or work as possible, and hence it becomes important to discover the least possible amount of heat or work that has to be used to effect a given separation. This value can then be used as a measure of the thermodynamic efficiency of any actual process.

It is readily apparent that in most distillation processes heat is being lost in various ways, for example, in the condenser cooling water or in the hot liquid leaving the bottom of the column, and that some of this heat might be saved by suitable heat exchangers. This again leads to the question: What is the least amount of heat (or work), assuming the process to be carried out in the most efficient manner possible? In general, heat and work both depend on the particular path, and one cannot calculate the minimum requirement of either without considering the process in detail. There is, however, one particular process—the isothermal reversible process—for which the work is measured by the change in the function A and hence is dependent only on the initial and

[1] OTHMER, D. F., *Ind. Eng. Chem.*, **27**, 250 (1935).

final states and not on the path. ΔA for the process gives the minimum possible work necessary to cause the given change by any isothermal process.

Suppose that one wished to calculate the minimum work to separate one mole of a liquid binary initial, or feed, solution of composition x_1 into two product solutions of compositions x_2 and x_3, respectively. Let us imagine the process carried out from the initial to the final states by a series of reversible isothermal steps as follows:

Step 1.   Vaporize the two components from the feed solution separately through semipermeable membranes at their respective equilibrium pressures and in the proportion to form the first product of composition x_2.

Step 2.   Compress the separated vapors to the equilibrium pressures of the components over the first-product solution.

Step 3.   Condense the vapors into this solution through semipermeable membranes.

Steps 4, 5, *and* 6   Carry out corresponding steps for transferring the two components from the feed to the second-product solution in a reversible manner.

The work terms for all the steps are then added; and if we assume gases are ideal and liquid volumes negligible, we obtain, per mole of feed,

$$W = -\Delta A = -RT \left[\frac{x_2(x_1 - x_3)}{x_2 - x_3} \ln \frac{\bar{p}_{A2}}{\bar{p}_{A1}} + \frac{(1 - x_2)(x_1 - x_3)}{x_2 - x_3} \ln \frac{\bar{p}_{B2}}{\bar{p}_{B1}} \right.$$
$$\left. + \frac{x_3(x_2 - x_1)}{x_2 - x_3} \ln \frac{\bar{p}_{A3}}{\bar{p}_{A1}} + \frac{(1 - x_3)(x_2 - x_1)}{x_2 - x_3} \ln \frac{\bar{p}_{B3}}{\bar{p}_{B1}} \right] \quad \text{(XIII.1)}$$

where subscripts 1, 2, and 3 refer to feed, first product, and second product, respectively, and subscripts A and B to the components. For the special case of separation into the two pure components, Eq. (XIII.1) reduces to

$$W = -RT \left[x_1 \ln \frac{p_{A1}}{\bar{p}_{A1}} + (1 - x_1) \ln \frac{p_{B1}}{\bar{p}_{B1}} \right] \quad \text{(XIII.2)}$$

Equations (XIII.1) and (XIII.2) can be further simplified for the case of ideal solutions, for which

$$\bar{p}_i = x_i p_i \quad \text{(XIII.3)}$$

Making this substitution in Eq. (XIII.2),

$$W = RT[x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1)] \quad \text{(XIII.4)[1]}$$

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[1] This equation follows directly from

$$W = \Delta E - T \Delta S$$

since $\Delta E = 0$ for an ideal solution. Strictly, it applies to a batch process, and the

In order to obtain the thermodynamic efficiency of an actual distillation process operated with the consumption of steam, it is suggested that the minimum steam requirement to produce the minimum work be calculated according to the methods of Chap. III.

Illustration 1.—Calculate the minimum work of separation of a 50 mole per cent solution of benzene and toluene into one product containing 95 per cent benzene and another containing 95 per cent toluene at the temperature of 25°C. Compare with the work to cause complete separation. Calculate the minimum steam requirement for complete separation if saturated steam at 50 lb. per sq. in. absolute pressure were used and the lowest temperature at which heat can be discharged is 70°F.

Assume benzene and toluene form an ideal solution.

$$x_1 = 0.500, \qquad x_2 = 0.950, \qquad x_3 = 0.050$$
$$R = 1.99, \qquad T = 298°K.$$

Substituting in Eq. (XIII.1),

$$W = -292 \text{ c.h.u./lb.-mole of feed}$$

For separation into pure components, substitution into Eq. (XIII.4) gives

$$W = -410$$

It is of interest to note that separation into 99 per cent products only increases the work to 308 so that there is a sharp increase in work requirement as pure products are approached.

From Chap. III the maximum work obtainable in a heat engine from a given quantity of steam is given by,

$$W_{max} = m(\Delta H - T_0 \, \Delta S)$$

where m = pounds of steam.
Using the Keenan-Keyes steam tables,

$$\Delta H = 1,136 \text{ B.t.u./lb.}$$
$$\Delta S = 1.5840 \text{ B.t.u./lb./°F.}$$
$$W_{max} = 410 \times 1.8 = 738 \text{ B.t.u./lb.-mole of feed}$$
$$m = \frac{738}{1,136 - 530 \times 1.584} \text{ lb./mole of feed} = 2.49$$

Since there are two moles of feed per mole of head product,

minimum steam requirement per mole of head product = 2×2.49 = 4.98 lb.

For a similar calculation applied to determination of the thermodynamic efficiency of a beer still, a paper by Weber[1] may be referred to.

INTEGRAL VAPORIZATION (OR CONDENSATION)

This type of distillation process has already been discussed in a qualitative way, and the next step is to develop equations for quantitative

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corresponding equation for a continuous process is

$$W = \Delta H - T \, \Delta S$$

but the difference between them is generally negligible.

[1] WEBER, H. C., *Trans. Am. Inst. Chem. Eng.*, **34**, 569 (1938

calculations.   The following treatment will be limited to the case of a single liquid phase.   The treatment in this and most of the subsequent sections of the chapter will be in terms of moles and mole fractions, but it should be noted that most, if not all, of the relationships obtained are equally valid for weights and weight fractions.
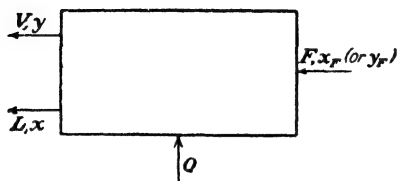
FIG. XIII.4.—Integral vaporization or condensation.

Binary System.—For either vaporization or condensation the elementary process is indicated in Fig. XIII.4, where F is the moles of feed liquid in the case of vaporization or moles of feed vapor in the case of condensation.   The process can be carried out either continuously or batchwise.   If continuous, the vapor flow may be either parallel or countercurrent to the liquid flow.   From the material balances,

$$F = L + V \tag{XIII.5}$$
$$F x_F = Lx + Vy \tag{XIII.6}$$

one obtains

$$\zeta_V \text{ (fraction vaporized)} = \frac{V}{F} = \frac{x - x_F}{x - y} \tag{XIII.7}$$

The relative amount of the two phases at the end of the process is given by the expression

$$\frac{V}{L} = \frac{x - x_F}{x_F - y} \tag{XIII.8}$$

The usual assumption for the batch process is that the vapor produced is in equilibrium with the residual liquid, or

$$y = \phi(x)$$

where $\phi(x)$ is the equilibrium relationship.   In the case of the continuous process there are two limiting cases: (1) equilibrium between vapor and residual liquid; (2) equilibrium between vapor and feed.   In an actual case the composition would probably lie in between these two limiting ones.

Equation (XIII.8) has a simple geometric interpretation that is often useful.   In Fig. XIII.1,

$$\frac{x - x_F}{x_F - y} = \frac{x_2 - x_1}{x_1 - y_2} = \frac{FE}{EG}$$

In other words, at any point in the two-phase region such as E or L, the perpendicular through the point cuts the horizontal tie line into segments

whose lengths are proportional to the amounts of the phases, the segment touching the vapor line representing the liquid phase, and vice versa.

For the case of integral condensation the corresponding equations are readily seen to be

$$\zeta_C = \frac{L}{F} = \frac{y - y_F}{y - x} \qquad \text{(XIII.9)}$$

and

$$\frac{L}{V} = \frac{y - y_F}{y_F - x} \qquad \text{(XIII.10)}$$

Multicomponent System.—The equations for a binary system are readily generalized to treat the case of any number of components. A total material balance gives, as before,

$$F = L + V \qquad \text{(XIII.5)}$$

and a balance on any component i,

$$x_{F_i}F = x_i L + y_i V \qquad \text{(XIII.11)}$$

Eliminating L,

$$\frac{V}{F} = \zeta_V = \frac{x_{F_i} - x_i}{y_i - x_i} \qquad \text{(XIII.12)}$$

or

$$y_i = \frac{x_{F_i} - x_i}{\zeta_V} + x_i \qquad \text{(XIII.13)}$$

Utilizing the equilibrium relation in the form

$$y_i = K_i x_i \qquad \text{(XII.71)}$$

one gets

$$y_i = \frac{x_{F_i}}{\zeta_V + (1/K_i)(1 - \zeta_V)} \qquad \text{(XIII.14)}$$

and since $\Sigma y_i = 1$, we have

$$\sum \frac{x_{F_i}}{\zeta_V + [(1 - \zeta_V)/K_i]} = 1 \qquad \text{(XIII.15)}^*$$

To make the meaning of Eq. (XIII.15) entirely clear, the following developed form is given for the case of a system of three components designated by A, B, and C:

$$\frac{x_{FA}}{\zeta_V + [(1 - \zeta_V)/K_A]} + \frac{x_{FB}}{\zeta_V + [(1 - \zeta_V)/K_B]} + \frac{x_{FC}}{\zeta_V + [(1 - \zeta_V)/K_C]} = 1 \qquad \text{(XIII.16)}$$

For the case of condensation, an entirely analogous derivation leads to a similar expression. In this case, it is a little better to use the relation

$$\Sigma x_i = 1$$

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* A different equation but one equally suitable for determination of ζ is obtained by using the condition $\Sigma x_i = 1$. In the case of Eq. (XIII.15) each term represents a residual-vapor composition; in the other case each term is a condensate composition.

and this leads to the equation

$$\sum \frac{y_{Fi}}{\zeta_c + K_i(1 - \zeta_c)} = 1 \qquad \text{(XIII.17)}$$

where y_{Fi} is the mole fraction of any component in the initial or feed vapor.

The individual terms in the summation are compositions of the condensed liquid. In order to obtain the composition of the residual vapor one can make a material balance on each component. The generalized balance equation is

$$y_{Fi} = y_{Vi}(1 - \zeta_c) + x_i \zeta_c \qquad \text{(XIII.18)}$$

For the special case of an ideal solution and ideal gas,

$$K_i = \frac{p_i}{p} \qquad \text{(XIII.19)}$$

and Eq. (XIII.15) becomes

$$\sum \frac{x_{Fi}}{\zeta_V + (p/p_i)(1 - \zeta_V)} = 1 \qquad \text{(XIII.20)}$$

with an analogous equation for condensation.

It should be noted that Eq. (XIII.17) is also applicable to the case where the condensable vapors are mixed with some noncondensable gas provided that the solubility of the latter in the condensate can be neglected.

Illustration 2.—What fraction of a liquid mixture containing 10 mole per cent propane, 65 per cent n-butane, and 25 per cent n-pentane would be vaporized in a flash-vaporization process at a temperature of 40°F. and a pressure of 600 mm. abs. in the flash chamber?

The assumption will be made that the liquid solutions are ideal and the vapor is an ideal gas. The following vapor-pressure data for 40°F. are available:

<div style="text-align:center">

Propane,   3,800 mm.

n-Butane,   820 mm.

n-Pentane,   190 mm.

</div>

Equation (XIII.20) is applicable, but a trial solution must be made to obtain ζ_V. For example, let $\zeta_V = 0.500$. Then, by Eq. (XIII.20),

$$\frac{0.100}{0.500 + \frac{600}{3800} \times 0.500} + \frac{0.650}{0.500 + \frac{600}{820} \times 0.500} + \frac{0.250}{0.500 + \frac{600}{190} \times 0.500}$$
$$= 0.173 + 0.750 + 0.120 = 1.043 \neq 1.00$$

After a few more trials, the solution is found to be

$$\zeta_V = 0.66 \text{ or } 66 \text{ per cent vaporized} \qquad \text{(mole per cent)}$$

It should be noted that the tacit assumption has been made that the process is isothermal. Actually a flash evaporation is more nearly adiabatic. The conditions

of this problem could be fulfilled by having the liquid mixture approach the expansion valve at some elevated temperature which could readily be calculated from the fact that enthalpy remains constant in the process.

Illustration 3.—Given a liquid containing 60 mole per cent benzene, 30 per cent toluene, and 10 per cent *m*-xylene, what would be the composition of the vapor if 50 mole per cent were vaporized by the process of integral vaporization at 1 atm. final pressure?

Vapor-pressure data are as follows:

Vapor pressure, mm. Hg	Temperature, °C.						
	60	70	80	90	100	110	120
Benzene..	...	540	756	1,008	1,338	1,740	2,215
Toluene....................	139	206	287	404	557	741	990
m-Xylene.........	51	78	116	168	238	330	449

As before, the assumption of ideal-liquid solution and ideal gas will be made. Equation (XIII.20) is again applicable; but now the temperature is the unknown, and a trial solution must be made with various temperatures. The corresponding vapor pressures are read from a plot of the above data.

Only the final trial will be given.

Let $t = 95°C$.

Vapor pressures are

> Benzene, 1,150 mm. Hg.
> Toluene, 477 mm. Hg.
> Xylene,   199 mm. Hg.

The mole fractions in the vapor are

> Benzene, 0.725.
> Toluene, 0.233.
> Xylene, 0.042.

The composition of the liquid is readily found from a material balance.

Illustration 4.—A solvent consisting of 50 per cent benzene, 30 per cent toluene, and 20 per cent *m*-xylene by volume is totally evaporated into a stream of heated air so that the resulting mixture contains 5.0 per cent solvent vapor by volume. The mixture is to be compressed to 60 lb. per sq. in. gauge and cooled at constant pressure to 20°C. The condensed solvent and residual gas become thoroughly mixed in passing from the condenser to the trap, where the condensate is separated and drawn off, so that the condensate may be assumed to be in equilibrium with the residual gas. Assuming that all mixtures of these three solvents are ideal, calculate the expected percentage recovery and the composition of the recovered solvent.

Vapor pressures at 20°C. are

> Benzene,   74 mm.
> Toluene,   22 mm.
> *m*-Xylene, 6.4 mm.

Densities in grams per cubic centimeter are

$$0.879 \text{ for } C_6.$$
$$0.866 \text{ for } C_7.$$
$$0.866 \text{ for } C_8.$$

Per 100 cc. of solvent,

$$\frac{50 \times 0.879}{78} \text{ moles } C_6 = 0.563$$

$$\frac{30 \times 0.866}{92} \text{ moles } C_7 = 0.282$$

$$\frac{20 \times 0.866}{106} \text{ moles } C_8 = 0.163$$

$$\text{Total moles} = \overline{1.008}$$

Mole fractions in initial gas are

$$C_6, \frac{0.563}{1.008} \times 0.0500 = 0.0280$$

$$C_7, \frac{0.282}{1.008} \times 0.0500 = 0.0140$$

$$C_8, \frac{0.163}{1.008} \times 0.0500 = 0.0081$$

$$p = \frac{74.7}{14.7} \times 760 = 3,840 \text{ mm.}$$

Substituting in Eq. (XIII.17) and using $K_i = p_i/p$,

$$\frac{0.0280}{\zeta_c + (74/3,840)(1 - \zeta_c)} + \frac{0.0140}{\zeta_c + (22/3,840)(1 - \zeta_c)} + \frac{0.0081}{\zeta_c + (6.4/3,840)(1 - \zeta_c)} = 1$$

$$\frac{0.0280}{\zeta_c + 0.01927(1 - \zeta_c)} + \frac{0.0140}{\zeta_c + 0.00572(1 - \zeta_c)} + \frac{0.0081}{\zeta_c + 0.001668(1 - \zeta_c)} = 1$$

Let $\zeta_c = 0.0400$.

$$0.479 + 0.307 + 0.1945 = 0.9805$$

$$\zeta_c = 0.0390$$

$$0.487 + 0.315 + 0.199 = 1.001$$

$$\therefore \frac{0.0390}{0.050} \times 100 = 78 \text{ per cent of the solvent is condensed}$$

Molal composition of the liquid is given by the three values of x that add to 1.00, *viz.*,

48.6 mole per cent benzene.
31.5 mole per cent toluene.
19.9 mole per cent xylene.

Vapor composition can be found from the equilibrium relation

$$y_i = \frac{p_i}{p} x_i$$

At the point of initial condensation (dew point) either for a mixture of condensable vapors or for a mixture of condensable vapors and non-condensable gases, $\zeta_c = 0$, and Eq. (XIII.17) becomes

$$\sum \frac{y_{Fi}}{K_i} = 1 \tag{XIII.21}$$

or, for the case of ideal solution and ideal gases,

$$p \sum \frac{y_{Fi}}{p_i} = 1 \tag{XIII.22}$$

These two equations can be used to calculate either the temperature or the pressure of initial condensation, given the other one. For pressure the calculation is straightforward, but for temperature it involves a trial process.

At the final condensation, or bubble point for a mixture with no noncondensable gas, the following relations hold:

$$\Sigma K_i y_{Fi} = 1 \tag{XIII.23}$$

and, for ideal gas, $\quad \dfrac{1}{p} \Sigma y_{Fi} p_i = 1 \tag{XIII.24}$

These follow at once by putting $\zeta_C = 1$ in the equation analogous to Eq. (XIII.17), which represents a summation of residual-vapor compositions.

Starting with a feed liquid, the bubble-point equation would be obtained from Eq. (XIII.15) by letting $\zeta_V = 0$, which gives

$$\Sigma K_i x_{Fi} = 1$$

DIFFERENTIAL VAPORIZATION (OR CONDENSATION)

Binary Solutions.—Since in this case the bulk of one phase is in equilibrium at any instant with only a small increment of the other phase, which is then removed from the scene, the quantitative treatment must be made by the use of calculus. As before, only the case of a single liquid phase will be treated.

Given L moles of liquid of composition x in a still at any instant, vaporize dL moles and let y be the composition of the vapor. A material balance on component A for this process gives

$$Lx = y\,dL + (x - dx)(L - dL) \tag{XIII.25}$$

or $\qquad \dfrac{dL}{L} = \dfrac{dx}{y - x} \tag{XIII.26}$

Integrating between limits,

$$\int_F^L \frac{dL}{L} = \int_{x_F}^{x_L} \frac{dx}{y - x} \tag{XIII.27}$$

$$\ln \frac{L}{F} = \ln \frac{F - V}{F} = \ln (1 - \zeta_V) = \int_{x_F}^{x_L} \frac{dx}{y - x} \quad \text{(XIII.28)}$$

The integration may be performed for equilibrium conditions when the equilibrium relationship $y = \phi(x)$ is known. For dilute solutions, Henry's law

$$y = kx$$

may be assumed, and Eq. (XIII.28) becomes

$$\ln (1 - \zeta_V) = \frac{1}{k - 1} \ln \frac{x_L}{x_F} \quad \text{(XIII.29)}$$

or

$$1 - \zeta_V = \left(\frac{x_L}{x_F}\right)^{\frac{1}{k-1}} \quad \text{(XIII.30)}$$

Using the relationship for ideal solutions when the vapor phase is an ideal gas, *viz.*, Eq. (XII.1), Eq. (XIII.28) can be readily developed to

$$\ln (1 - \zeta_V) = \frac{1}{\alpha - 1} \ln \frac{x_L(1 - x_F)}{x_F(1 - x_L)} + \ln \frac{1 - x_F}{1 - x_L} \quad \text{(XIII.31)}$$

This equation is correct only for an isothermal process, but it can also be used for an isobaric process with an arithmetic average value of α since, as was shown in the preceding chapter, the variation in α is not great.

An exactly similar treatment in the case of differential condensation leads to the equations

$$\ln (1 - \zeta_C) = - \int_{y_F}^{y_V} \frac{dy}{y - x} \quad \text{(XIII.32)}$$

$$\ln (1 - \zeta_C) = - \frac{1}{k - 1} \ln \frac{y_V}{y_F} \quad \text{(XIII.33)}$$

and

$$\ln (1 - \zeta_C) = - \frac{1}{\alpha - 1} \ln \frac{y_V(1 - y_F)}{y_F(1 - y_V)} - \ln \frac{y_V}{y_F} \quad \text{(XIII.34)}$$

which are the analogues of Eqs. (XIII.28), (XIII.29), and (XIII.31).

It is perhaps well to emphasize at this point that these equations apply to an idealized limiting case in which the distillation is conducted at an infinitely slow rate (equilibrium) and in which there is no refluxing of liquid after the vapor has left the boiling liquid and no entrainment of liquid in the vapor. In any actual distillation in the laboratory or the plant, this limiting condition is approached only more or less closely.

Illustration 5.—One hundred pounds of a 1 per cent solution by weight of furfural in water is to be concentrated by differential distillation at atmospheric pressure. What weight of the solution must be distilled in order to obtain 99 per cent of the total furfural in the distillate? What will be the composition of this distillate?

Data on equilibrium for this system at 1 atm. are as follows:

Per Cent by Weight of Furfural in the Liquid	Per Cent by Weight of Furfural in the Vapor
0.20	1.5
0.40	3.0
0.60	4.4
0.80	5.8
1.00	7.0

Assuming the relation $y = kx$

the average value of k is 7.32. Equation (XIII.29) applies in this case, and

$$x_F = 0.0100$$
$$x_L = \frac{0.00010}{1 - \zeta_V}$$

Substituting in Eq. (XIII.29),

$$\log (1 - \zeta_V) = \frac{1}{6.32} \log \frac{0.01}{1 - \zeta_V}$$
$$1 - \zeta_V = 0.533$$

46.7 per cent of the solution must be distilled.

Concentration of furfural in the distillate $= \frac{0.99}{46.7} \times 100$ per cent $= 2.12$ per cent

Illustration 6.—Plot curves showing composition of residue, of total distillate and boiling point, against weight per cent distilled for the differential vaporization at 1 atm. of a 60 weight per cent solution of benzene in toluene.

It may be assumed that Eq. (XIII.31) applies in this case, and an average value of $\alpha = 2.50$ will be used. The following sample calculation will show the method.

Let $x_L = 0.400.$*

Substituting values in Eq. (XIII.31),

$$\zeta_V = 0.611$$

Composition of the total distillate is readily obtained from a material balance as follows:

$$x_F = x_L(1 - \zeta_V) + x_D \zeta_V$$

where x_D is the composition of the distillate. Then,

$$x_D = \frac{x_F - x_L(1 - \zeta_V)}{\zeta_V}$$

For the case where $x_L = 0.400$,

$$x_D = 0.727$$

The boiling point of any liquid in the still is obtained by the method outlined in Illustration 3 of Chap. XII.

By assuming a series of values of x_L the data for the curves are obtained, and these have been plotted in Fig. XIII.5.

In cases where there is no simple algebraic equation expressing the equilibrium relationship, the right-hand sides of Eqs. (XIII.28) and

* x is used to denote weight fraction in this illustration.

(XIII.32) may readily be integrated by plotting $1/(y - x)$ as ordinate against x or y as the case may be and finding the area under the curve between the given limits of x or y.

Vaporization or condensation of systems involving two liquid phases is of considerable practical as well as theoretical interest but is considered beyond the scope of this book.
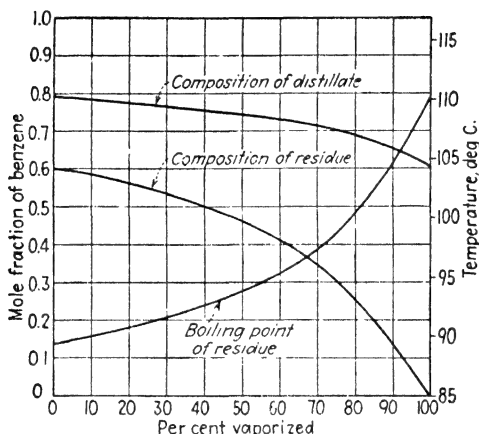
Fig. XIII.5.—Differential distillation curves for the system benzene-toluene.

Multicomponent Systems.— Assume the equilibrium relation to be of the form given by Eq. (XII.71), *viz.*,

$$y_i = K_i x_i$$

and choose one component of the system, say component B, as a reference. Let the solution to be subjected to a differential vaporization contain L_i moles of any component and L_B moles of the reference component. Vaporize a differential amount of the liquid producing a vapor containing dL_i moles of i and dL_B moles of B. For equilibrium we must have

$$\frac{y_i}{y_B} = \frac{K_i}{K_B} \frac{x_i}{x_B} \tag{XIII.35}$$

or

$$\frac{dL_i}{dL_B} = \frac{K_i}{K_B} \frac{L_i}{L_B} \tag{XIII.36}$$

or

$$d \ln L_i = \frac{K_i}{K_B} d \ln L_B \tag{XIII.37}$$

One of these equations can be written for each component with the exception of B. In general, as was shown in the preceding chapter, K is a complex function of p, t and the composition; but if we assume an ideal-liquid solution, K is a function of p and t only. The ratio of any two values of K changes very little with p and t and as a first approxi-

mation Eq. (XIII.37) can be integrated on the assumption that the K ratio is constant, giving

$$\log \frac{L_i}{F_i} = \frac{K_i}{K_B} \log \frac{L_B}{F_B} \qquad \text{(XIII.38)}$$

If the vapor is an ideal gas,

$$\frac{K_i}{K_B} = \frac{p_i}{p_B} \qquad \text{(XIII.39)}$$

Equations (XIII.38) and (XIII.39) can be combined and put in the form

$$\log \frac{(1 - \zeta_V)x_{Li}}{x_{Fi}} = \alpha_{iB} \log \frac{(1 - \zeta_V)x_{LB}}{x_{FB}} \qquad \text{(XIII.40)}$$

where $\alpha_{iB} = K_i/K_B$ or p_i/p_B.
Material balance gives the equation

$$x_{Fi} = x_{Li}(1 - \zeta_V) + y_i\zeta_V \qquad \text{(XIII.41)}$$

where y_i is the mole fraction of any component in the total combined distillate. There will be $n - 1$ equations of the form of Eq. (XIII.40), n equations like Eq. (XIII.41) and the equation

$$\Sigma x_{Li} = 1 \qquad \text{(XIII.42)}$$

or a total of $2n$ equations from which one can solve by trial to obtain the composition of the distillate and the residue, given the feed-liquid composition, the pressure, and the fraction vaporized.

The basic equation for condensation, analogous to Eq. (XIII.38) for vaporization, is

$$\frac{K_i}{K_B} \log \frac{V_i}{F_i} = \log \frac{V_B}{F_B} \qquad \text{(XIII.43)}$$

or

$$\alpha_{iB} \log \frac{V_i}{F_i} = \log \frac{V_B}{F_B} \qquad \text{(XIII.44)}$$

By the same procedures used for vaporization, one obtains

$$\alpha_{iB} \log \frac{(1 - \zeta_C)y_{Vi}}{y_{Fi}} = \log \frac{(1 - \zeta_C)y_{VB}}{y_{FB}} \qquad \text{(XIII.45)}$$

$$y_{Fi} = y_{Vi}(1 - \zeta_C) + x_i\zeta_C \qquad \text{(XIII.46)}$$

$$\Sigma y_{Vi} = 1 \qquad \text{(XIII.47)}$$

Illustration 7.—A vapor mixture containing 30 mole per cent *n*-hexane, 30 per cent *n*-heptane, and 40 per cent *n*-octane is partially condensed at atmospheric pressure. Assuming ideal gas and ideal solution, compare the composition of the residual vapor for the case of condensation of 80 per cent of the total moles when the condensation is (1) integral and (2) differential.

Vapor pressures may be calculated from the equation

$$\log p(\text{mm.}) = A - \frac{B}{T(^\circ\text{K.})}$$

using the following values for the constants:[1]

Hydrocarbon	A	B
Hexane..................................	7.7215	1,654.6
Heptane.......	7.5917	1,750.0
Octane...........	7.7503	1,941.4

Some vapor-pressure values are as follows:

t°C.	$p(C_6)$	$p(C_7)$	$p(C_8)$, mm. Hg
90	1,462	592	253
95	1,690	689	299
100	1,935	798	352
105	2,209	916	411
110	2,526	1,056	482

For integral condensation, Eq. (XIII.17) applies. For this special case its form is

$$\frac{y_{FA}}{\varsigma_C + (p_A/p)(1 - \varsigma_C)} + \frac{y_{FB}}{\varsigma_C + (p_B/p)(1 - \varsigma_C)} + \frac{y_{FC}}{\varsigma_C + (p_C/p)(1 - \varsigma_C)} = 1$$

Final temperature of condensation is the unknown variable in this case, and a trial solution is indicated. Assuming $t = 95^\circ$C. and substituting values in the equation just given,

$$0.241 + 0.305 + 0.455 = 1.001$$

This trial so nearly satisfies the equation that no further trials are necessary. Each term in the equation represents a mole fraction of one of the components in the condensed liquid. The composition of the residual vapor may be calculated from Eq. (XIII.18), giving the following results:

$y_{VA} = $ mole fraction hexane in residual vapor $= 0.535$

$y_{VB} = $ mole fraction heptane in residual vapor $= 0.280$

$y_{VC} = $ mole fraction octane in residual vapor $= 0.180$

These figures may be adjusted slightly if desired to satisfy the condition $\Sigma y_{Vi} = 1$. In the case of differential condensation, since the equilibrium temperature varies throughout the process, one must choose an average at which to evaluate α. In this connection it is generally helpful to calculate the initial and final temperatures for the whole condensation process, which may readily be done with the aid of Eqs. (XIII.22) and (XIII.24), using a trial process. The approximate values are as follows:

Initial condensation point $= 108^\circ$C.

Final condensation point $= 93^\circ$C.

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[1] BEATTY, H. A., and G. CALINGAERT, *Ind. Eng. Chem.*, **26**, 904 (1934).

Since α does not vary greatly with the temperature, only an approximate value is necessary, and for this problem we shall assume a temperature of 100°C.

$$\alpha_{AB} = \frac{1,935}{798} = 2.42$$

$$\alpha_{CB} = \frac{352}{798} = 0.441$$

Applying Eq. (XIII.45) to this case, we get the two equations

$$\log y_{VA} = 0.413 \log y_{VB} + 0.103$$
$$\log y_{VC} = 2.27 \log y_{VB} - 0.093$$

For trial solution, assume $y_{VB} = 0.250$.

Substitution of this value in the two equations gives

$$y_{VA} = 0.717, \qquad y_{VC} = 0.035$$
$$\Sigma y_V = 1.002$$

This is sufficiently close to unity so that no further trials are necessary.

The following tabulation summarizes the results of the comparison:

Process	Mole per cent of component in the residual vapor		
	C_6	C_7	C_8
Integral condensation	54	28	18
Differential condensation.................	72	25	3

It can be concluded that a differential condensation gives a considerably higher enrichment of the vapor than an integral condensation.

Differential Condensation in Presence of Inert Gas.—It will be assumed at once that we are dealing with ideal liquid solutions and ideal gases and that the inert gas is not soluble in the condensate to an appreciable extent. The basic equation is the same as Eq. (XIII.44), and this is readily transformed to

$$\alpha_{iB} \log \frac{(1 - \zeta_c y_F) y_{Vi}}{y_{Fi}} = \log \frac{(1 - \zeta_c y_F) y_{VB}}{y_{FB}} \qquad \text{(XIII.48)}$$

where y_F is the mole fraction of total condensable vapor at the start and ζ_c is the fraction of the total condensable that is condensed. Equation (XIII.47) no longer applies to this case, but in its place we have

$$\sum \frac{y_{Vi}}{p_i} = \frac{1}{p} \qquad \text{(XIII.49)}$$

This is derived as follows:

For the final increments of condensate the following equation must be true,

$$\Sigma x_i = 1 \qquad \text{(XIII.50)}$$

and for phase equilibrium between an ideal solution and an ideal gas,

$$x_i p_i = y_{vi} p \qquad (XIII.51)$$

Combining Eqs. (XIII.50) and (XIII.51) gives Eq. (XIII.49).

A total material balance on condensable vapor gives

$$y_F(1 - \zeta_c) = (1 - \zeta_c y_F) \Sigma y_{vi} \qquad (XIII.52)$$

By trial solution of Eqs. (XIII.48), (XIII.49), and (XIII.52) one can calculate the fraction condensed and the composition of the residual vapor, given the pressure and the final temperature in the condenser. The average composition of the condensate is obtained by material balances on the individual components, which give equations of the type

$$y_{Fi} = (1 - \zeta_c y_F) y_{vi} + x_i \zeta_c y_F \qquad (XIII.53)$$

where x_i is the average mole fraction of any component in the total condensate.

STEAM DISTILLATION

This is a general term applied to any process of vaporizing a liquid by injecting steam into it so that a direct contact between steam and boiling liquid occurs. It has the effect of a distillation at a reduced pressure since the steam balances part of the total pressure on the system and thereby permits the distillation to occur at a lower temperature. The same end could be accomplished by maintaining a reduced pressure with a vacuum pump, but in cases of relatively nonvolatile substances that must be distilled at a low enough temperature to avoid decomposition this is difficult to accomplish in practice. It is sometimes advantageous to steam-distill at a reduced pressure, in other words, to combine steam and vacuum distillation.

As far as the general principle is concerned, one could just as well use some inert gas instead of steam, but the latter has certain practical advantages that have resulted in its universal adoption for this purpose.

Steam distillation finds considerable application in the separation of liquids of low volatility from nonvolatile material and in the removal of solvents and other volatile liquids from solution in relatively non-volatile oils or from solid adsorbents. The treatment in this chapter is confined to the estimation of the minimum steam requirement for a few special cases.

Case I: Single Liquid Immiscible with Water; Temperature above the Three-phase Boiling Point.—This statement regarding the boiling point generally implies that the heat necessary for distillation comes from a source other than the direct steam; usually it is supplied by indirect steam in a coil or jacket. By utilizing superheated steam it is also possible

to distill at a temperature above the three-phase boiling point and yet supply all the heat from the direct steam.

If p_A and p_W are the vapor pressures of the liquid to be distilled and of water, respectively, at the given temperature, then, according to the stated conditions,

$$p < p_A + p_W$$

and no water layer will be present in the still.

Assume that the liquid is maintained at a constant temperature by suitable means and that the steam comes into such thorough contact with the liquid that the mixed vapor leaving is in equilibrium with the liquid. Then the following equations hold provided that the vapor is an ideal gas and the liquid contains no dissolved substance that appreciably affects its vapor pressure

$$y_A p = p_A \qquad \text{(XIII.54)}$$

$$y_W = 1 - y_A = 1 - \frac{p_A}{p} \qquad \text{(XIII.55)}$$

Dividing one equation by the other,

$$\frac{y_A}{y_W} = \frac{p_A}{p - p_A} = \frac{N_A}{N_W} \qquad \text{(XIII.56)}$$

Then,

$$\frac{m_W}{m_A} = \frac{N_W M_W}{N_A M_A}$$

$$= \frac{M_W}{M_A} \frac{p - p_A}{p_A} \qquad \text{(XIII.57)}$$

This shows that the steam consumption in pounds of steam per pound of substance distilled will be lowered as the pressure is lowered and will be lowered by an increase in the temperature or an increase in the molecular weight.

Illustration 8.—It is desired to distill acetophenone at atmospheric pressure without formation of a water layer, using only the direct steam as the source of heat. The steam is to be taken from a supply of saturated steam at elevated pressure and expanded to 1 atm. for use. What steam pressure would be necessary, and what would be the minimum steam consumption? It is desirable to keep the pressure as low as possible. Neglect heat losses. Assume that the acetophenone is preheated to the distillation temperature.

It will be assumed that the acetophenone distills at a constant equilibrium temperature determined by the fact that the heat given up by the steam in cooling to this temperature will equal the heat of vaporization. The lowest temperature at which distillation could take place without formation of a water layer is about 100°C. For the present illustration this temperature will be assumed to be the distillation temperature.

Vapor pressure of acetophenone:[1]

$$t = 202.4°C., \qquad p = 760 \text{ mm.}$$
$$t = 80.0°C., \qquad p = 10 \text{ mm.}$$

Corresponding boiling points of water are 100 and 11.3°C., respectively. Plotting these data as a Dühring line (see page 249), the vapor pressure at 100°C. is estimated to be 25 mm.

By Eq. (XIII.57),

$$\frac{m_W}{m_A} = \frac{18}{120} \times \frac{760 - 25}{25} = 4.4 \text{ lb. steam per lb. acetophenone}$$

The latent heat of vaporization of acetophenone at 100°C. may be estimated from a plot of the Hildebrand function (see Chap. IX), assuming it to belong in the class of the hydrocarbons. This gives the value 98 cal. per g. or 176 B.t.u. per lb.

Each pound of steam must supply 176/4.4, or 40, B.t.u. in cooling from its expanded state to 100°C.

Enthalpy of saturated steam at 1 atm. = 1,150.4 B.t.u./lb.
Enthalpy required in expanded steam = 1,150.4 + 40 = 1,190.4

This corresponds to saturated steam at 120 lb. per sq. in. abs. (expansion at constant *H*). Therefore, saturated steam at this pressure if expanded to 1 atm. will be sufficiently superheated so that it can supply the necessary heat of vaporization by cooling to 100°C.

The steam requirement will decrease as the distillation temperature is increased; but as the steam consumption decreases, the necessary steam pressure rises very rapidly owing to the very small change in the enthalpy of saturated steam with pressure. In fact, the maximum enthalpy of saturated steam is 1,205 B.t.u. per lb., which occurs at about 450 lb. per sq. in.

Case II: Single Liquid Immiscible with Water; Temperature Is the Three-phase Boiling Point.

—Unless means are provided for supplying the heat for distillation either indirectly or directly through the use of superheated steam as in Illustration 8, there will be two liquid phases and distillation will take place at the three-phase boiling point where

$$p = p_A + p_W$$

and Eq. (XIII.57) becomes

$$\frac{m_W}{m_A} = \frac{M_W}{M_A} \frac{p_W}{p_A} \qquad (XIII.58)$$

To determine the distillation temperature, one can plot $p_A + p_W$ vs. the temperature and read off the temperature corresponding to the total pressure p. It is obvious that the upper temperature limit for such a distillation is the boiling point of water under the given pressure.

Equations (XIII.57) and (XIII.58) give, not the total steam consumption for the distillation, but only the steam that is used as a car-

[1] PERRY, J. H., "Chemical Engineers' Handbook," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

rier or an entraining agent. In addition, there may be some steam used to supply the sensible heat of the liquid and the latent heat of vaporization.

Effect of Pressure.—This will depend on the way in which p_W/p_A changes with the temperature. An approximate idea of the effect can be obtained from the Clausius-Clapeyron equation and Trouton's rule.

From Eq. (VI.46),

$$\ln \frac{p_2}{p_1} = \frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Applying this to two different substances,

$$\left(\frac{p_W}{p_A}\right)_2 = \left(\frac{p_W}{p_A}\right)_1 e^{\frac{L_W - L_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \tag{XIII.59}$$

But, as a rough approximation based on Trouton's rule,

$$L_W = L_A$$

if T_W and T_A are approximately equal, and therefore

$$\left(\frac{p_W}{p_A}\right)_2 = \left(\frac{p_W}{p_A}\right)_1$$

This indicates that, over small ranges at least, the carrier steam consumption will be approximately independent of the pressure and there can be no great advantage in changing the pressure. Experimental data show that, for liquids less volatile than water, p_W/p_A decreases with the temperature and therefore an increase in the pressure will decrease, to some extent, the weight of direct steam used per unit of distillate.

Case III: Single Liquid Partially Miscible with Water.—This case is not essentially different from the immiscible case, the only difference being that the vapor pressures to use in Eqs. (XIII.57) and (XIII.58) would not be those of the pure substances but would be obtained from a phase diagram such as Fig. XII.31 or calculated by the methods indicated in Chap. XII (page 568). If the liquid were appreciably miscible with water at the condensation temperature, as is the case with aniline, for example, there would be an appreciable loss unless some means were used to recover the material dissolved in the water layer. This can be done either by a process of rectification or by extraction with a suitable liquid.

Case IV: Batch Distillation of Solution of a Volatile Liquid in a Non-volatile One.—Assume that the temperature is constant and above the three-phase boiling point so that no water layer is present. For the equilibrium vapor at any instant,

$$\frac{dN_W}{dN_A} = \frac{p - \bar{p}_A}{\bar{p}_A} \tag{XIII.60}$$

where p is the total pressure and $\bar{p}_A$ the partial pressure of the volatile component A in the vapor in equilibrium with the liquid.

Now,
$$\frac{N_A}{N_B} = \frac{x}{1 - x} \tag{XIII.61}$$

where x is the mole fraction of A in the liquid and B refers to the non-volatile component.

Since N_B is a constant,

$$dN_A = N_B \frac{dx}{(1 - x)^2} \tag{XIII.62}$$

and
$$dN_W = N_B \frac{p - \bar{p}_A}{\bar{p}_A} \frac{dx}{(1 - x)^2} \tag{XIII.63}$$

or
$$N_W = N_B p \int_{x_1}^{x_1} \frac{dx}{\bar{p}_A (1 - x)^2} - N_B \int_{x_1}^{x_1} \frac{dx}{(1 - x)^2} \tag{XIII.64}$$

From Eq. (XIII.64) the steam consumption for distillation between any given composition limits at constant temperature and total pressure can be obtained by a graphical integration if one has data on $\bar{p}_A$, that is, on the vapor pressure of the solution as a function of the concentration. For the special case of ideal solution,

$$\bar{p}_A = p_A x$$

Substituting this in Eq. (XIII.64) and integrating,

$$\frac{N_W}{N_B} = \frac{p}{p_A} \ln \frac{x_1(1 - x_2)}{x_2(1 - x_1)} - \frac{p - p_A}{p_A} \left(\frac{1}{1 - x_2} - \frac{1}{1 - x_1} \right) \tag{XIII.65}[1]$$

Case V : Continuous Distillation of a Volatile Liquid from Solution in a Nonvolatile One in a Countercurrent Tower.—From a material balance over the whole column (Fig. XIII.6),

$$N_W = N_B \frac{X_2 - X_1}{Y_2 - Y_1} \tag{XIII.66}$$

or, from section CC to the bottom,

$$N_W = N_B \frac{X - X_2}{Y - Y_2} \tag{XIII.67}$$

Equation (XIII.67) can be put in the form

$$Y = \frac{N_B}{N_W} X + Y_2 - \frac{N_B}{N_W} X_2 \tag{XIII.68}$$

[1] The derivation of this equation is somewhat simpler if one expresses concentration in the units used in the next case.

This is a relation between the compositions of the two streams that pass in the tower. On a YX diagram it is a straight line[1] and will be designated as an "operating line." Another relation between Y and X is the phase-equilibrium relation, which in general terms may be written

$$Y = \phi(X) \qquad \text{(XIII.69)}$$

and must satisfy the terminal conditions

$$X = 0, \qquad Y = 0$$

The plot of this relationship on a YX diagram will be known as the "equilibrium line." The steam requirement as moles of steam per mole
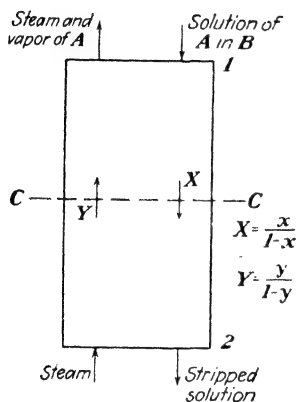
Fɪɢ. XIII.6.—Diagram for Case V.
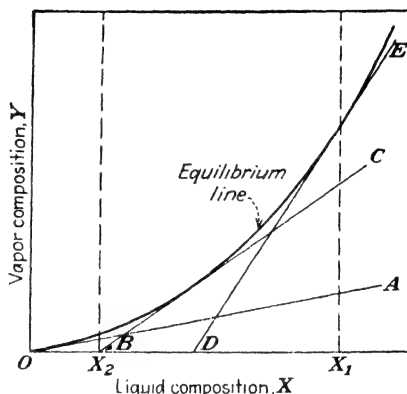
Fɪɢ. XIII.7.—Minimum steam requirement for the continuous distillation of a volatile liquid from solution in a nonvolatile one in a countercurrent tower.

of solvent B, or N_W/N_B, is the reciprocal of the slope of the operating line [see Eq. (XIII.68)]. The minimum steam requirement will correspond to the operating line of maximum slope for the given conditions. The maximum slope is determined by the fact that no operating line can cross the equilibrium line because that would constitute a violation of the second law since it would call for the generation of a vapor with a higher content of the solute than the equilibrium one. Consequently, the operating line of maximum slope is one that is tangent to the equilibrium curve. Three such lines are shown in Fig. XIII.7 for the usual case where the steam to the tower is free of the component being distilled, or $Y_2 = 0$. Operating line BC is the one for minimum steam requirement when the solution is to be stripped to the composition X_2. OA is the line for complete stripping of the solute from the solution, and DE is the line for

[1] This is the reason for the choice of these concentration units instead of x and y.

equilibrium between entering solution and exit vapors.   In all cases, the composition of the exit vapors is given by the intersection of the operating line with the ordinate at X_1.

Special Case of Ideal Solution.—For such a solution,

$$yp = xp_A$$

and since

$$y = \frac{Y}{1 + Y}$$

and

$$x = \frac{X}{1 + X}$$

the equilibrium relation Eq. (XIII.69) takes the forms

$$Y = \frac{Xp_A}{p - (p_A - p)X} \tag{XIII.70}$$

and

$$X = \frac{Yp}{p_A - (p - p_A)Y} \tag{XIII.71}$$

The equilibrium curve has a positive curvature (as in Fig. XIII.7) when $p_A > p$ (the usual case in distillation) and is asymptotic to the ordinate $X = p/(p_A - p)$.   When $p_A < p$, the curvature is negative and the asymptote is the abscissa $Y = p_A/(p - p_A)$; when $p = p_A$, the equilibrium curve is a straight line.

Let Y_t, X_t be the coordinates at the point of tangency between an operating line and the equilibrium line.   The slope of the operating line at this point is

$$\frac{Y_t}{X_t - X_2} \tag{XIII.72}$$

The slope of the equilibrium line is

$$\frac{dY}{dX} = \frac{p_A p}{[p - (p_A - p)X_t]^2} \tag{XIII.73}$$

and these two slopes are equal, or

$$Y_t = \frac{(X_t - X_2)p_A p}{[p - (p_A - p)X_t]^2} \tag{XIII.74}$$

Since Y_t, X_t is on the equilibrium curve, Eq. (XIII.70) applies; and, eliminating Y_t between Eqs. (XIII.70) and (XIII.74),

$$X_t = \sqrt{\frac{pX_2}{p_A - p}} \tag{XIII.75}$$

Substituting for X_t in Eq. (XIII.73) and noting that

$$\frac{N_W}{N_B} = \frac{1}{(dY/dX)}$$

we have

$$\left(\frac{N_W}{N_B}\right)_{\min} = \frac{p - 2\sqrt{pX_2(p_A - p)} + X_2(p_A - p)}{p_A} \quad \text{(XIII.76)}$$

When $X_2 = 0$ (complete stripping),

$$\left(\frac{N_W}{N_B}\right)_{\min} = \frac{p}{p_A} \quad \text{(XIII.77)}$$

Equations (XIII.76) and (XIII.77) also apply to the case where the equilibrium is given by Henry's law in the form

$$yp = xk_A$$

Illustration 9.—A solution of benzene in a mineral oil is to be steam-distilled at atmospheric pressure to recover the benzene. Compare the minimum steam requirement for (a) a batch process and (b) a continuous countercurrent process, expressed as pounds of steam per gallon of benzene recovered.

Data and assumptions are as follows:

1. The rich oil solution contains 5 per cent benzene by weight.
2. The stripped solution is to contain 0.10 per cent by weight.
3. Temperature to be maintained at 110°C. by indirect steam.
4. The oil solution may be assumed ideal, taking molecular weight of the oil at 225.
5. Initial temperature of oil solution is 20°C.
6. Specific heat of the oil is 0.50 B.t.u. per lb. per °F.
7. Steam is available at 25 lb. gauge pressure.

Mole fraction of benzene in the rich solution:

$$x_1 = \frac{\frac{5}{78}}{\frac{5}{78} + \frac{95}{225}} = 0.132$$

Mole fraction of benzene in the lean solution:

$$x_2 = \frac{0.10/78}{(0.10/78) + (99.9/225)} = 0.00288$$

p_A = vapor pressure of benzene at 110°C. = 1,748 mm.

Substituting in Eq. (XIII.65) for the batch distillation,

$$\frac{N_W}{N_B} = \frac{760}{1,748} 2.303 \log_{10} \frac{0.132 \times 0.9971}{0.00288 \times 0.868} - \frac{760 - 1,748}{1,748}\left(\frac{1}{0.9971} - \frac{1}{0.868}\right)$$
$$= 1.641 \text{ moles steam per mole oil}$$

$$\text{Moles benzene recovered per mole oil} = \frac{0.132}{0.868} - \frac{0.00288}{0.997} = 0.149$$

$$\text{Gallons benzene per mole oil} = \frac{0.149 \times 78}{7.34} = 1.585$$

$$\text{Lb. steam per gal. benzene recovered} = \frac{1.641 \times 18}{1.585} = 18.6$$

This is the direct, or open, steam required. Indirect, or closed, steam is necessary to heat the charge in the still to 110°C. and vaporize the benzene.

The mean specific heat of benzene over this range is 0.45 B.t.u. per lb. per °F. The latent heat of vaporization at 110°C. is estimated by the rule of Kistiakowsky[1] or of Watson[2] to be 6,750 g.-cal. per g.-mole.

Per mole of oil, the heat required will be

$$\left(220 \times 0.50 + \frac{0.132}{0.868} \times 78 \times 0.45\right)(110 - 20)1.8 + \frac{0.132}{0.868} \times 6,750 \times 1.8$$
$$= 20,600 \text{ B.t.u.}$$

$$\text{Lb. steam per gal. benzene} = \frac{20,600}{934 \times 1.585} = 13.9$$

Total steam requirement for the batch process = 32.5 lb./gal. For the continuous process, the open steam is given by Eq. (XIII.76). Thus,

$$X_2 = \frac{0.00288}{0.997} = 0.00289$$

$$\frac{N_W}{N_B} = \frac{760 - 2\sqrt{760 \times 0.00289(1,748 - 760)} + 0.00289(1,748 - 760)}{1,748}$$
$$= 0.383 \text{ moles steam per mole oil}$$
$$= 4.35 \text{ lb. steam per gal.}$$

The open steam is much less for the continuous than for the batch distillation. The closed-steam requirement would be the same without heat recovery, but with the continuous process a large portion of the sensible and latent heats can be recovered in heat exchangers.

It is of interest to note that the open steam for complete stripping in the continuous process is

$$\frac{760}{1,748} \times \frac{18}{1.585} = 4.94 \text{ lb. steam per gal.}$$

whereas in the batch process it would be infinite according to the equation.

RECTIFICATION

The columns or towers in which rectification is commonly carried out are of two general types, (1) packed and (2) plate. Reference should be made to texts on the unit operations for the construction of each, but the essential difference between the two for the purpose of this book is that the composition and temperature of the two countercurrent streams of fluid change in a continuous manner by differential steps in the packed column and in a discontinuous curve with finite steps in the plate column. Each tray, or plate, of the latter column holds a pool of liquid through which the vapor bubbles. The average composition and temperature of the liquid on each plate differ by a finite amount from those of the liquids on the trays above and below. As the number of plates increases or as the reflux ratio increases, the plate column, in general, approaches the packed column in its action and at the limit, *i.e.*, infinite plates or total reflux, the two are substantially identical in principle.

[1] Chap. IX, p. 378.
[2] Chap. IX, p. 378.

A rectification system consists of the column proper, a boiler (also called a "still" or "reboiler") to produce a vapor feed to the bottom of the column, and a condenser to produce a liquid reflux for the top of the column. In all cases, the column itself is substantially adiabatic (heat loss in large lagged columns is very small) and all heat transfers take place in the boiler and condenser.

Rectifying columns may be operated either batchwise or continuously. In the former case, a charge of the liquid to be separated is placed in the boiler, and the only feed to the column is the vapor from the boiler, which is continually changing in composition. In a continuous column, a fluid to be separated flows in continuously at an intermediate point known as the "feed level." The section of column above this level is known as the "enriching section" and that below it as the "exhausting section." From the condenser above the column a head product in which the more volatile components have been concentrated is withdrawn continuously, and a bottom product rich in the less volatile components is continuously taken off from the boiler. It is also possible to have separate continuous enriching or exhausting columns, the chief difference being that the former receives a vapor feed and the latter a liquid feed.

The application of thermodynamics to the rectifying column has two main purposes, as follows:

1. The determination of the theoretical number of steps in a plate column necessary for a given set of conditions. For the packed column the corresponding quantity would be the height of the column equivalent to a theoretical step, or unit.

2. The determination of the minimum heat or work required.

We shall next proceed to the development of quantitative relationships necessary to accomplish these purposes, limiting the treatment to binary systems of completely miscible liquids.

The Theoretical, or Equilibrium, Plate.—The common definition of a theoretical plate is that it is a plate holding a pool of liquid from which rises a vapor of uniform composition in phase equilibrium with a liquid whose composition is the average of that of the liquid leaving the plate, assuming it were thoroughly mixed. This sets up a standard with which to compare actual plates. Departure of actual plates from the ideal is due to two main causes, (1) insufficient contact between the vapor and liquid to permit a close approach to phase equilibrium and (2) nonuniformity of liquid composition on the plate, coupled with the fact that the overflow liquid does not represent the average composition of the liquid on the plate.

Plate Efficiency.—This is a measure of the extent to which the actual plate departs from the ideal. It is defined in several different ways, the commonest definition being that of over-all plate efficiency, which is the

number of theoretical plates necessary for a given separation with a given set of conditions, divided by the actual number of plates that is giving the separation in question.   An individual plate efficiency, sometimes called "Murphree efficiency," is defined by the equation

$$e = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}} \tag{XIII.78}$$

where y_{n-1} = average composition of actual vapor rising from the $(n - 1)$ plate (plate below the nth).

y_n = the same for the nth plate.

y_n^* = composition of vapor in phase equilibrium with the average liquid overflowing from the nth plate.

The numerator of Eq. (XIII.78) gives the actual enrichment of the vapor in a given component, and the denominator gives the maximum possible enrichment.[1]   Equation (XIII.78) as given defines an average efficiency for the whole plate, but it can also be used to define an efficiency over any small area of a plate; in this case it is called a "point," or "local," efficiency.   The ordinary single-plate efficiency is obviously an average, obtained by a process of integration, of all the local efficiencies.

A discussion of the various factors that affect the plate efficiency is beyond the scope of this book, but it is desirable to point out that, whereas the local efficiency can never exceed 100 per cent, the other two efficiencies can and often do exceed this figure.   This appears at first thought to be a violation of the second law, but it is simply due to the fact that in large towers there may exist a considerable concentration gradient in the liquid so that the average liquid on the plate is appreciably richer than the overflow liquid, with the result that the vapor rising may have a composition greater than that for phase equilibrium with the overflow liquid.   This question has been studied by several investigators; their papers should be consulted for further details.[2]

Theoretical Performance in a Packed Column.—This is commonly expressed in two ways, (1) height equivalent to a theoretical plate (H.E.T.P.) and (2) height of a transfer unit (H.T.U.).   H.E.T.P. is simply the length of a section of the column that accomplishes the same degree of enrichment as a theoretical plate.   To put it in slightly different form, it is a length of packing such that the average vapor leaving the top is in phase equilibrium with the average liquid leaving the bottom.   There is no corresponding simple physical interpretation of the meaning

[1] A similar efficiency could be defined on the basis of liquid-phase compositions. Though it might be useful under certain conditions it has not been used to any extent.

[2] HAUSEN, H., *Forsch. Gebiete Ingenieurw.*, **7**, 177 (1936).   KIRSCHBAUM, E., *Ibid.*, **8**, 63 (1937).   LEWIS, W. K., JR., *Ind. Eng. Chem.*, **28**, 399 (1936).

of H.T.U. The mathematical definition of H.T.U. is given by the equation[1]

$$\text{H.T.U.} = \frac{H_p}{\int_{y_1}^{y_2} dy/(y^* - y)} \qquad \text{(XIII.79)}$$

where H_p is total height of packing and y_1 and y_2 are the terminal vapor compositions. The integral is called the number of transfer units and is equal to the area under the curve of $1/(y^* - y)$ vs. y between the given limits.

In general, the number of theoretical plates and the number of transfer units will be different. This will be discussed quantitatively later in this chapter (page 637). Although H.E.T.P. has been much more commonly used to characterize the packed tower, the use of H.T.U. rests on a sounder theoretical basis since it considers a differential rather than a stepwise process.

General Equations for Adiabatic Rectifying Columns.—Considering first the section of the column above the feed level (see Fig. XIII.8), we may write material and energy balances for the portion of the system included between the sections AA' and BB' as follows:

$$V_n = O_n + D \qquad \text{(over-all material balance)} \qquad \text{(XIII.80)}$$
$$V_n y = O_n x + D x_D \qquad \text{(balance of component } A\text{)} \qquad \text{(XIII.81)}$$
$$V_n H = O_n h + D h_D + Q_c \qquad \text{(over-all energy balance)} \qquad \text{(XIII.82)}$$

To make the three equations symmetrical, write Eq. (XIII.82) in the form

$$V_n H = O_n h + D h'_D \qquad \text{(XIII.83)}$$

where

$$h'_D = h_D + \frac{Q_c}{D} = h_D + q_c \qquad \text{(XIII.84)}$$

Eliminating V_n from Eqs. (XIII.80) and (XIII.81),

$$y = \frac{O_n}{O_n + D} x + \frac{D}{O_n + D} x_D \qquad \text{(XIII.85)}$$

The masses can be entirely eliminated from this equation in the following way: Eliminating V_n between Eqs. (XIII.80) and (XIII.81) and then between Eqs. (XIII.80) and (XIII.83), we get the two equations

$$\frac{O_n}{D} = \frac{x_D - y}{y - x} \qquad \text{(XIII.86)}$$

$$\frac{O_n}{D} = \frac{h'_D - H}{H - h} \qquad \text{(XIII.87)}$$

A ratio such as O_n/D is known as a "reflux ratio."

[1] A similar equation can be written in terms of liquid compositions but it is generally assumed in distillation that the vapor film offers the controlling resistance.

Equating Eqs. (XIII.86) and (XIII.87),

$$\frac{x_D - y}{y - x} = \frac{h'_D - H}{H - h} \tag{XIII.88}$$

or $\qquad y = \dfrac{h'_D - H}{h'_D - h}\, x + \dfrac{H - h}{h'_D - h}\, x_D \tag{XIII.89}$

Equations (XIII.85) and (XIII.89) are relations between the compositions of the vapor stream and liquid stream which pass at any level in
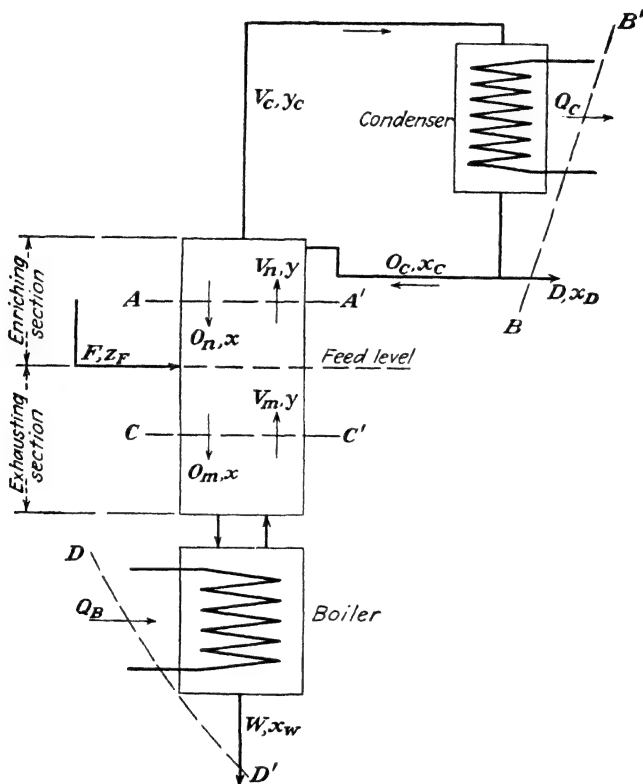
Fig. XIII.8.—Diagram of a rectification system.

the column and are entirely general and therefore free from assumptions other than that the column is operating in a steady state and is adiabatic. Such a relation is known as the "equation of the operating line." Equation (XIII.89) may be put in another form as follows:

$$Q_c = V_c(H_c - h_D) \tag{XIII.90}$$
$$V_c = O_c + D \tag{XIII.91}$$

Combining these two equations with Eq. (XIII.84),

$$h'_D = h_D + \left(\frac{O_C}{D} + 1\right)(H_C - h_D) \qquad \text{(XIII.92)}$$

The particular reflux ratio O_C/D is of special significance and will be represented by R. It is the one usually meant when the term is used without further qualification. The relation between q_C and the reflux ratio is readily obtained from Eqs. (XIII.84) and (XIII.92), thus:

$$q_C = (R + 1)(H_C - h_D) \qquad \text{(XIII.93)}$$

From Eqs. (XIII.92) and (XIII.89),

$$y = \frac{(H_C - h_D)R - (H - h) + (H_C - h)}{(H_C - h_D)R + (H_C - h)} x$$
$$+ \frac{H - h}{(H_C - h_D)R + (H_C - h)} x_D \quad \text{(XIII.94)}$$

The operating line [Eq. (XIII.89) or (XIII.94)] is fixed once the product composition and reflux ratio are known. Whether the line can be plotted or not depends on whether or not the enthalpies are known as a function of composition at the given pressure.

Equations for the section of the column below the feed level can be obtained in an entirely analogous manner by balancing between sections CC' and DD'. The fundamental balance equations are

$$O_m = V_m + W \qquad \text{(XIII.95)}$$
$$O_m x = V_m y + W x_W \qquad \text{(XIII.96)}$$
$$O_m h + Q_B = V_m H + W h_W \qquad \text{(XIII.97)}$$

Proceeding as before, the following equations are readily obtained:

$$y = \frac{O_m}{O_m - W} x - \frac{W}{O_m - W} x_W \qquad \text{(XIII.98)}$$

$$\frac{y - x_W}{H - h'_W} = \frac{x - x_W}{h - h'_W} \qquad \text{(XIII.99)}$$

where

$$h'_W = h_W - \frac{Q_B}{W} = h_W - q_B \qquad \text{(XIII.100)}$$

or

$$y = \frac{h'_W - H}{h'_W - h} x + \frac{H - h}{h'_W - h} x_W \qquad \text{(XIII.101)}$$

This is the equation of an operating line for the exhausting section of the column. From over-all balances on the entire system the following set of equations is obtained:

$$F = D + W \qquad \text{(XIII.102)}$$
$$F z_F = D x_D + W x_W \qquad \text{(XIII.103)}$$
$$F I_F + Q_B = D h_D + W h_W + Q_C \qquad \text{(XIII.104)}$$

Equation (XIII.104) can be put in the form

$$FI_F = Dh'_D + Wh'_W \qquad \text{(XIII.105)}$$

The symbols z_F and I_F have been used to denote the composition and enthalpy, respectively, of the feed because, in the general case, the feed may be either a vapor or a liquid or a mixture of the two. From Eqs. (XIII.102) and (XIII.103)

$$\frac{D}{W} = \frac{z_F - x_W}{x_D - z_F} \qquad \text{(XIII.106)}$$

and

$$\frac{F}{W} = \frac{x_D - x_W}{x_D - z_F} \qquad \text{(XIII.107)}$$

From Eqs. (XIII.102), (XIII.103), and (XIII.105), there is obtained

$$\frac{z_F - x_W}{x_D - z_F} = \frac{I_F - h'_W}{h'_D - I_F} \qquad \text{(XIII.108)}$$

From Eqs. (XIII.84), (XIII.92), (XIII.100), (XIII.104), (XIII.106), and (XIII.107),

$$h'_W = \frac{(x_D - x_W)I_F - (z_F - x_W)(R+1)H_C + (z_F - x_W)h_D}{x_D - z_F} \qquad \text{(XIII.109)}$$

From Eqs. (XIII.101) and (XIII.109) it is evident that the operating line for the exhausting section is fixed once the reflux ratio, the state of the feed, and the compositions of head product and bottom product are fixed. From Eqs. (XIII.98), (XIII.102), (XIII.106), and (XIII.107),

$$\frac{O_m}{D} = \left(\frac{y - x_W}{y - x}\right)\left(\frac{x_D - z_F}{z_F - x_W}\right) \qquad \text{(XIII.110)}$$

This is a reflux-ratio equation for the exhausting section analogous to Eq. (XIII.86) for the enriching section.

Fig. XIII.9.—Relation between overflows at different levels.
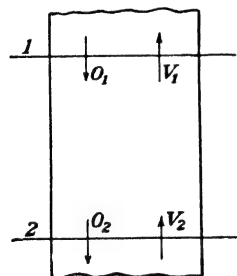
In the case of a column that has no enriching section, a liquid feed enters at the top and the usual balances lead to

$$\frac{F}{W} = \frac{y_F - x_W}{y_F - x_F} \qquad \text{(XIII.111)}$$

where subscript F now refers to the top of the column. The ratio F/W is a reflux ratio for a stripping column.

If we consider any two levels in a column between points where fluids enter or leave the column (see Fig. XIII.9), the following three balance equations can be written:

$$V_1 + O_2 = V_2 + O_1 \qquad \text{(XIII.112)}$$
$$V_1 y_1 + O_2 x_2 = V_2 y_2 + O_1 x_1 \qquad \text{(XIII.113)}$$
$$V_1 H_1 + O_2 h_2 = V_2 H_2 + O_1 h_1 \qquad \text{(XIII.114)}$$

Eliminating the two V's,

$$\frac{O_2}{O_1} = \frac{(H_1 - h_1)(y_1 - y_2) + (H_2 - H_1)(y_1 - x_1)}{(H_2 - h_2)(y_1 - y_2) + (H_2 - H_1)(y_2 - x_2)} \qquad \text{(XIII.115)}$$

It is clear that, in general, O_2 does not equal O_1; in other words, the quantity of overflow liquid is not a constant in any section of the column. A similar relation exists between V_1 and V_2.

Special Cases.—A number of these general equations can be very simply represented on an enthalpy-concentration diagram, but before considering the more general case certain special cases will be treated for which the general equations may be greatly simplified.

Case I: Heat of Mixing and Difference in Sensible Heat Are Negligible.— This assumption leads to

$$h = h_D = h_F = h_W \qquad \text{(XIII.116)}$$

and

$H - h$ = latent heat of vaporization at constant composition of the vapor
$$= L_A y + L_B (1 - y) \qquad \text{(XIII.117)}$$

Making these substitutions in Eq. (XIII.94) and solving for y,

$$y = \frac{[L_M(R + 1) - L_B]x + L_B x_D}{L_M(R + 1) + (L_A - L_B)(x - x_D)} \qquad \text{(XIII.118)}$$

where
$$L_M = L_A y_C + L_B(1 - y_C) \qquad \text{(XIII.119)}$$

With data available on the latent heats of vaporization of the individual components, the operating line for the enriching section can readily be determined from Eq. (XIII.118). A similar equation can be derived for the exhausting column from Eqs. (XIII.101) and (XIII.109).

Case II: Identical Molal Latent Heats.—This is in addition to the assumptions of case I and is based on the fact that many pairs of similar liquids have approximately the same molal latent heat of vaporization as demanded by Trouton's rule. Substitution of

$$L_A = L_B = L$$

in Eq. (XIII.118) leads to

$$y = \frac{R}{R + 1} x + \frac{x_D}{R + 1} \qquad \text{(XIII.120)}$$

Also, since
$$H_1 = H_2$$
and
$$H_1 - h_1 = H_2 - h_2$$
Eq. (XIII 715) reduces to
$$O_2 = O_1 \qquad \text{(XIII.121)}$$

or the *molal* liquid overflow in the column is a constant. From Eq. (XIII.112) it is also evident that

$$V_2 = V_1$$

This special case is commonly referred to as one of constant molal overflow.
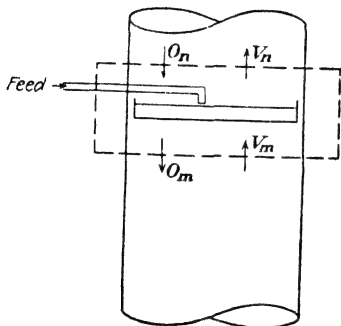
FIG. XIII.10.—Feed-level balance.

The equation of the operating line (XIII.120) is now that of a straight line of slope $R/(R + 1)$ and intercept on the y axis of $x_D/(R + 1)$. In order to obtain a similar simple equation for the exhausting section it will be necessary to consider in detail the state of the feed.

Effect of State of the Feed.—Consider a section of a plate column around the feed level as shown in Fig. XIII.10, and make material and energy balances over the section as follows:

$$F + O_n + V_m = O_m + V_n \qquad \text{(XIII.122)}$$
$$lFh_F + (1 - l)FH_F + O_n h_n + V_m H_m = O_m h_m + V_n H_n \qquad \text{(XIII.123)}$$

where l is the fraction of the feed that is liquid. Assume constant enthalpies of saturated vapor and liquid, or

$$H_m = H_n = H$$
and
$$h_m = h_n = h$$

and eliminate V_m and V_n between Eqs. (XIII.122) and (XIII.123), giving the equation

$$O_m - O_n = F\left(\frac{H - H_F}{H - h} + l\frac{H_F - h_F}{H - h}\right) \qquad \text{(XIII.124)}$$
$$= qF \qquad \text{(XIII.125)}$$

Where q, as the equation shows, is the quantity of heat required to bring one mole of the feed to the state of saturated vapor, divided by the molal latent heat. This may be most easily visualized by considering several special cases.

Case 1.   Feed is a superheated vapor.

$$l = 0$$
$$q = \frac{H - H_F}{L}$$

q is negative, and $H - H_F$ represents the heat that must be removed from the vapor to bring it to the saturated state.

Case 2. Feed is a saturated vapor.

$$l = 0 \qquad H = H_F$$
$$\therefore q = 0$$

Case 3. Feed is a mixture of vapor and liquid.

$$H = H_F \qquad h = h_F \qquad q = l$$

Case 4. Feed is a saturated liquid.

$$H = H_F \qquad h = h_F \qquad l = 1 \qquad q = 1$$

Case 5. Feed is a liquid below the boiling point.

$$q = \frac{H - h_F}{H - h}$$

Substitution of Eq. (XIII.125) into (XIII.98) gives

$$y = \frac{O_n + qF}{O_n + qF - W} x - \frac{W}{O_n + qF - W} x_W \qquad \text{(XIII.126)}$$

Eliminating the masses in terms of the compositions by means of Eqs. (XIII.106) and (XIII.107) and introducing the reflux ratio R for O_n/D, this equation becomes

$$y = \frac{R + E_1 q}{R + E_1 q - E_2} x - \frac{E_2}{R + E_1 q - E_2} x_W \qquad \text{(XIII.127)}$$

where

$$E_1 = \frac{x_D - x_W}{z_F - x_W}$$

and

$$E_2 = \frac{x_D - z_F}{z_F - x_W}$$

Eqs. (XIII.126) and (XIII.127) are more directly useful equations of the exhausting line than Eq. (XIII.98) since the overflow in the exhausting section is not directly known but must be obtained from that in the enriching section. For case 4 of feed condition, which is probably the usual one, Eq. (XIII.126) can be written

$$y = \frac{O_n + F}{O_n + D} x - \frac{W}{O_n + D} x_W \qquad \text{(XIII.128)}$$

For the case of constant molal overflow this can be put in the following form, involving only mass ratios:

$$y = \frac{R + R_F}{R + 1} x - \frac{R_W}{R + 1} x_W \qquad \text{(XIII.129)}$$

Like the analogous equation for the enriching section, this gives a straight line on a yx diagram. For an exhausting column alone, the corresponding

equation is

$$y = \frac{R_E}{R_E - 1} x - \frac{x_W}{R_E - 1} \qquad \text{(XIII.130)}$$

Utilizing Eqs. (XIII.106) and (XIII.107) and noting that $z_F = x_F$ for this special case, Eq. (XIII.129) can be put in the following useful form:

$$y = \frac{Rx_F + x_D - (R + 1)x_W}{(R + 1)(x_F - x_W)} x + \frac{(x_F - x_D)x_W}{(R + 1)(x_F - x_W)} \qquad \text{(XIII.131)}$$

Intersection of the Operating Lines.—Since these are lines of different slope, they must intersect and at the point of intersection the following conditions must be met:

$$y_m = y_n = y_i$$
$$x_m = x_n = x_i$$

Eliminating O_n between Eqs. (XIII.86) and (XIII.126) and substituting the conditions for the point of intersection, one gets

$$D(x_D - y_i) = qF(x_i - y_i) + W(y_i - x_W) \qquad \text{(XIII.132)}$$

Combining this with Eqs. (XIII.102) and (XIII.103),

$$y_i = \frac{q}{q - 1} x_i - \frac{z_F}{q - 1} \qquad \text{(XIII.133)}$$

This is the equation of a straight line that is the locus of the points of intersection of the two operating lines. It is a line that passes through the point

$$y_i = x_i = z_F$$

and has the slope $q/(q - 1)$. The various locus lines corresponding to the five cases of feed condition are shown in Fig. XIII.11 on a yx diagram.

Use of Fictitious Molecular Weight.—Since

$$L_A = M_A\lambda_A$$
and $$L_B = M_B\lambda_B$$

the condition of equal molal latent heats is satisfied if

$$M_B = M_A \frac{\lambda_A}{\lambda_B} \qquad \text{(XIII.134)}$$

We can arbitrarily satisfy this condition by assigning to component B a fictitious molecular weight as demanded by Eq. (XIII.134). The fictitious mole fraction of A in the solution is given by,

$$x = \frac{m_A/M_A}{(m_A/M_A) + (m_B/M_B)} \qquad \text{(XIII.135)}$$

Substituting for M_B from Eq. (XIII.134) and introducing weight fraction r, one gets

$$x = \frac{r\lambda_A}{r\lambda_A + (1 - r)\lambda_B} \qquad \text{(XIII.136)}$$

If mole fractions are calculated for any system from this equation, then the simplified equations applicable to the case of constant molal overflow can be used. It should be noted, however, that this procedure still involves the assumption of negligible heat of solution and negligible differences in sensible heat and so is not a correct substitute for the general equations. It should also be noted that if the equilibrium relation is of the form given by Eq. (XII.1) it is independent of the molecular weights and hence does not change when a fictitious molecular weight is used.

Number of Theoretical Plates.— The determination of this number is the usual application of the equations that have been developed for rectifying columns. It might be noted, however, that it is not the only one. There is a relation between the feed state and composition, the two product compositions, the reflux ratio (or some other mass ratio), and the number of theoretical sections, or plates; and the relationship can be used to calculate any one of these quantities, given the others. For

Fig. XIII.11.—Loci of the intersections of the operating lines.
1. $q < 0$, slope is positive, intercept is positive (superheated vapor feed)
2. $q = 0$, slope is zero (saturated vapor feed)
3. $q > 0 < 1$, slope is negative (liquid and vapor feed)
4. $q = 1$, slope is infinite (saturated liquid feed)
5. $q > 1$, slope is positive, intercept negative (subcooled liquid feed)

example, one might have a column already available and wish to determine what product composition is obtainable under a given set of conditions. The methods of calculation, whether for number of plates or one of the other variables, might be divided into the two general classes of (1) graphical methods and (2) analytical methods. The graphical methods may be further subdivided into those based on a yx diagram and those based on an enthalpy—concentration (Hx) diagram. All these methods will yield identical results if the basic assumptions are the same; the choice between them is largely one of convenience or individual preference.

It seems to the author that some have gone to unwarranted refinements in calculating number of plates and that there has been much

hairsplitting over fractional plates.   Keeping in mind the use to which a calculation of number of theoretical plates is to be put is helpful in preventing one from going to unjustified extremes in making such a calculation.   Thus, most of the calculations so made are later combined with very rough, assumed figures on plate efficiency to arrive at the number of actual plates.   Furthermore, there are other disturbing factors such as the fact that most systems are more complex than assumed in the calculations, the fact that the equilibrium data used are often not too accurate or the system is not adiabatic, etc.   In cases where a series of plate calculations is made purely for comparative purposes to show the effect of some variable, there may be some justification for considering fractional plates.
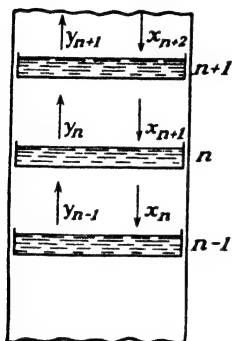
Fig. XIII.12.—Diagram of a section of a plate column.

The general principle involved in the calculation of number of plates is best illustrated by reference to Fig. XIII.12, which is a purely diagrammatic representation of a section of a column containing three plates.   The various liquid and vapor compositions have subscripts to designate the plate of origin of the fluid to which they refer.   Assume for the moment that the composition x_{n+2} of the liquid descending to the $n + 1$ plate is known.   The composition of the vapor rising from this plate can then be calculated from the equation of the operating line since such an equation relates the compositions of the streams that pass at any given level.   If y_{n+1} is known, the composition of the liquid leaving this plate, x_{n+1}, is obtained from the phase-equilibrium relationship since the definition of a theoretical plate requires that these two streams be in equilibrium.   From x_{n+1}, y_n is obtained from the operating line, then x_n from the equilibrium curve, etc., down the column in a stepwise manner. In order to start this process one must have some one known composition and a value for the reflux ratio in order to fix the operating line.   The product composition x_D will usually be given as one of the fixed conditions of the problem (in case it is one of the unknowns, a trial value can be assumed, which can later be checked), and this equals x_C if the condensation is total.   If it is partial, x_C must be calculated from the conditions obtaining in the condenser by some of the equations already given.

We shall next consider how the reflux ratio is to be obtained.

Reflux Ratio.—Equation (XIII.86) relates the reflux ratio at any level in the enriching section to the composition of the product and of the passing streams.   The $y - x$ difference is not definitely fixed but does have quite definite limits.   Since the vapors in the column are everywhere produced by vaporization of liquids, it is clear that the composition

of the vapor can never exceed that for phase equilibrium with the liquid from which it originated; otherwise, the second law would be violated. The composition of this liquid must obviously be less (only by a differential amount at the limit) than that of the liquid descending from above which is passing the vapor in question, and therefore one can conclude that $y - x$ has a maximum value corresponding to that for phase equilibrium. Conversely, the descending liquid is produced by condensation of vapor, and the limiting case of total condensation would give $y = x$; hence, the lower limit of $y - x$ is zero.
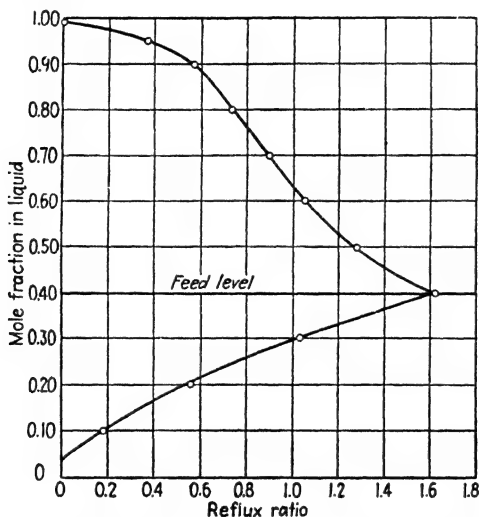
Fɪɢ. XIII.13.—Variation of minimum reflux ratio, O_n/D, with level in a column.

The maximum value of $y - x$ determines a minimum value of O_n/D (reflux ratio) for every level in the enriching section [Eq. (XIII.86)]. In Fig. XIII.13 this value has been plotted for the system benzene-toluene, assuming an average α of 2.50 and a head product of 99 mole per cent benzene. It shows that the minimum reflux ratio for the enriching section steadily increases as one progresses down the column and would be a maximum at whatever level is chosen as the feed level. The minimum reflux ratio O_m/D below the feed level was calculated by Eq. (XIII.110), assuming the feed to be a saturated liquid. In order to make the values comparable with those for the enriching section, F/D was subtracted from them, giving values of O_n/D. The behavior shown by the figure is typical of most systems, but in certain cases the maximum value of the minimum reflux may occur at some higher level.

In an adiabatic column the amount of reflux at various levels is not under control but, on the contrary, is fixed by the maximum amount

required at any level to satisfy the phase-equilibrium condition. This maximum value of the various minima is the least possible value for the level in question (usually the feed level) but is not necessarily the same as R ($= O_C/D$) because the overflow is not constant in the general case. To obtain the minimum O_C/D from the minimum O_n/D, use can be made of Eq. (XIII.115).

Thus, suppose that the maximum of the minima is 2.00 and occurs at the feed level and that O_C/O_F by Eq. (XIII.115) = 1.20. The minimum possible value of R would be $2.00 \times 1.20 = 2.40$, and this value is designated the "minimum reflux ratio." By combination of Eqs. (XIII.86) and (XIII.115) an equation for direct calculation of minimum reflux ratio $R_{\min}$ could be obtained. The value of R to be used in Eqs. (XIII.94) and (XIII.118) must be greater than this minimum or equal to it at the limit. For the special case of constant molal overflow,

$$\frac{O_n}{D} = \frac{O_C}{D}$$

and the minimum reflux ratio is a constant independent of level in the column. The value of R in Eq. (XIII.120) must be greater than this minimum. If equal to it, the given separation will require an infinite number of plates; if less, the separation is not possible. As the ratio is increased above the minimum, the number of plates required will decrease and reach a minimum value when the rising vapor is totally refluxed or when $R = \infty$. Upon putting this value of R in Eq. (XIII.94), the equation of the operating line reduces to

$$y = x \tag{XIII.137}$$

or the liquid and vapor streams passing in the column are identical in composition. The reflux ratio to use in establishing the operating lines will lie somewhere between the minimum and infinity. Its value is quite arbitrary and can be fixed only by economic considerations.

McCabe-Thiele Graphical Method.—The stepwise procedure for determination of number of plates can be done analytically with the two equations, one for the operating relation and one for the equilibrium relation, or it can be done graphically from a plot of these two lines on a yx diagram. The special case of constant molal overflow was first considered in detail by McCabe and Thiele[1] in 1925. Since this method is fully treated in at least two well-known texts on chemical engineering, a detailed treatment will be omitted here. It is desirable to point out, however, that the same method can be used for the general case or other special cases in which the operating lines are not linear. The lines can readily be plotted if the necessary enthalpy data are available. Since

[1] McCabe, W. L., and E. W. Thiele, *Ind. Eng. Chem.*, **17**, 605 (1925).

such data are available on but very few systems, and since the departure from linearity is small in the great majority of cases and in any case can be largely corrected by the method of a fictitious molecular weight, the use of the simple McCabe-Thiele method is practically universal.

In the case of liquids that have very similar properties, such as isomers and isotopes, and therefore require a large number of plates for separation, the graphical method becomes very tedious and certain algebraic methods are preferable.

Algebraic Methods.—In developing the methods of the following sections it is assumed that the liquid solutions are ideal and the vapor is an ideal gas; hence, the equilibrium relationship is given by Eq. (XII.1). This should be a valid assumption for most systems that require a large number of plates. A very simple equation is obtained for the case of total reflux as follows:

Starting at the bottom plate (No. 1) of the whole column, we have

$$\frac{y_1}{1 - y_1} = \alpha \frac{x_1}{1 - x_1}$$

but since, for total reflux, $\qquad x_2 = y_1$

then

$$\frac{x_2}{1 - x_2} = \alpha \frac{x_1}{1 - x_1}$$

or $\qquad X_2 = \alpha X_1$

Similarly,

$$\frac{y_2}{1 - y_2} = Y_2 = \alpha X_2 = X_3$$

or $\qquad X_3 = \alpha^2 X_1$

Then $\qquad X_4 = \alpha^3 X_1$

or, generalizing for an n-plate column,

$$\frac{X_n}{X_1} = \alpha^{n-1} \qquad\qquad\text{(XIII.138)}$$

When reflux is produced in a total condenser,

$$X_D = Y_n = \alpha X_n$$

Substituting in Eq. (XIII.138)

$$\frac{X_D}{X_1} = \alpha^n$$

or

$$n = \frac{\log (X_D/X_1)}{\log \alpha} \qquad\qquad\text{(XIII.139)}$$

If E = over-all fractionation factor = X_D/X_W,

$$n = \frac{\log E}{\log \alpha} - 1 \qquad\qquad\text{(XIII.140)}$$

If the reflux is produced in a partial condenser equivalent to one theoretical plate,

$$n = \frac{\log E}{\log \alpha} - 2 \qquad \text{(XIII.141)}$$

Equation (XIII.139) can also be written

$$\frac{y_n}{1 - y_n} = \alpha^n \frac{x_1}{1 - x_1} \qquad \text{(XIII.142)}$$

which is an equation for n equilibrium plates analogous to the equation

$$\frac{y}{1 - y} = \alpha \frac{x}{1 - x}$$

for any single plate.

In the more general case where the reflux ratio is finite, several methods of treatment have been developed. In those cases where the equilibrium curve lies relatively close to the diagonal and hence the operating lines are approximately parallel to the equilibrium curve, it can be shown that the number of theoretical plates and the number of transfer units are nearly the same; hence, one can calculate number of plates by the equations developed for transfer units. For example, assuming the case of equal latent heats, differentiation of Eq. (XIII.120) gives,

$$dy = \frac{R}{R + 1} dx \qquad \text{(XIII.143)}$$

Substituting Eqs. (XIII.143) and (XIII.120) into the equation

$$n \text{ (number of transfer units)} = \int_{y_1}^{y_2} \frac{dy}{y^* - y} \qquad \text{(XIII.144)}$$

there is obtained

$$n = \int_{x_r}^{x_D} \frac{dx}{y^* - x - \frac{1}{R}(x_D - y^*)} \qquad \text{(XIII.145)}$$

with a similar equation for the exhausting section. This equation was developed and applied by Lewis[1] to distillation calculations a number of years before the introduction of the transfer-unit concept. He performed the integration graphically. Dodge and Huffman[2] related y^* to x by the ideal-solution law [Eq. (XII.1)] and also by Henry's law and integrated algebraically, obtaining explicit expressions for the number of transfer units, which they assumed to be the same as the number of plates. Their paper should be consulted for further details.

[1] LEWIS, W. K., *Ind. Eng. Chem.*, **14**, 492–497 (1922).

[2] DODGE, B. F., and J. R. HUFFMAN, *Ind. Eng. Chem.*, **29**, 1434 (1937).

Smoker[1] developed an ingenious method for an analytic determination of number of plates that is best explained by reference to Fig. XIII.14. The basis for his calculations is a translation of the coordinate axes so that the origin is located at the point of intersection of the operating line
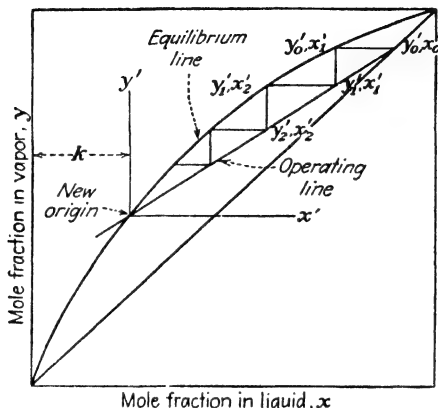
Fig. XIII.14. —Smoker's method for determination of the number of plates.

and the equilibrium line. If the equations of the operating line and equilibrium line are, respectively,

$$y = mx + b \qquad \text{(XIII.146)}$$

and

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \qquad \text{(XII.1)}$$

they become, when referred to the new axes,

$$y' = mx' \qquad \text{(XIII.147)}$$

and

$$y' = \frac{\alpha x'}{c^2 + c(\alpha - 1)x'} \qquad \text{(XIII.148)}$$

where $c = 1 + (\alpha - 1)k$.

k is the x coordinate of the new origin and is readily obtained by solution of the quadratic equation resulting from the elimination of y between Eqs. (XIII.146) and (XII.1).

Start the usual stepwise procedure at the point y_0', x_0' on the operating line, which in the case of the enriching section would be the composition of the vapor leaving the top plate, assuming reflux is produced in a total condenser. The composition of the liquid on that plate is given by the equilibrium equation

$$x_1' = \frac{c^2 y_0'}{\alpha - c(\alpha - 1)y_0'} \qquad \text{(XIII.149)}$$

[1] SMOKER, E. H., *Trans. Am. Inst. Chem. Eng.*, **34**, 165–172 (1938).

[a rearrangement of Eq. (XIII.148)]; but since

$$y_0' = mx_0'$$

then

$$x_1' = \frac{mc^2 x_0'}{\alpha - mc(\alpha - 1)x_0'} \qquad \text{(XIII.150)}$$

Similarly,

$$x_2' = \frac{mc^2 x_1'}{\alpha - mc(\alpha - 1)x_1'} \qquad \text{(XIII.151)}$$

or, combining Eqs. (XIII.150) and (XIII.151),

$$x_2' = \frac{m^2 c^4 x_0'}{\alpha^2 - mc(\alpha - 1)(\alpha + mc^2)x_0'} \qquad \text{XIII.152)}$$

One can continue to proceed in this stepwise fashion; but it soon becomes evident that the process can be generalized, giving

$$x_n' = \frac{m^n c^{2n} x_0'}{\alpha^n - mc(\alpha - 1)\dfrac{\alpha^n - m^n c^{2n}}{\alpha - mc^2} x_0'} \qquad \text{(XIII.153)}$$

Solving for n, one obtains the following equation for number of plates in either section of a column:

$$n = \frac{\log [x_0'(1 - Mx_n')/x_n'(1 - Mx_0')]}{\log (\alpha/mc^2)} \qquad \text{(XIII.154)}$$

where

$$M = \frac{mc(\alpha - 1)}{\alpha - mc^2}$$

When reflux is total, $m = 1$ and $k = 0$; hence, $c = 1$ and $M = 1$ and Eq. (XIII.154) reduces to

$$n = \frac{\log (X_0/X_n)}{\log \alpha} \qquad \text{(XIII.155)}$$

which is the same (including the boiler as one plate) as Eq. (XIII.139) already derived for this special case.

A variant of Smoker's method can be based on the total reflux case in which the operating line is the diagonal $y' = x'$. The operating line can be made the diagonal in the general case by first translating the axes to the point of intersection as in Smoker's method and then rotating them through an angle θ which is $45° - \phi$, where ϕ is the angle between the operating line and the original x axis. From the well-known relations for rotation of axes, x' based on the new axes may be related to x, and the combination of this relation with Eq. (XIII.155) gives an equation for n that is applicable to the general case. The derivation of this equation is an interesting exercise that is left to the ingenuity of the reader.

Thomson and Beatty[1] derived simplified equations for calculating the number of theoretical plates for the special case where one of the components is present to the extent of 5 mole per cent or less in the feed. Their method is based on the assumption of linear operating and equilibrium lines and uses a stepwise summation similar to that of the Smoker method.

Number of Plates vs. Number of Transfer Units.—We are now in a position to make a quantitative comparison between these two concepts. It has sometimes been erroneously stated that the two numbers were substantially the same whenever the number of units was large. The relation between them can be visualized with the aid of Fig. XIII.15.
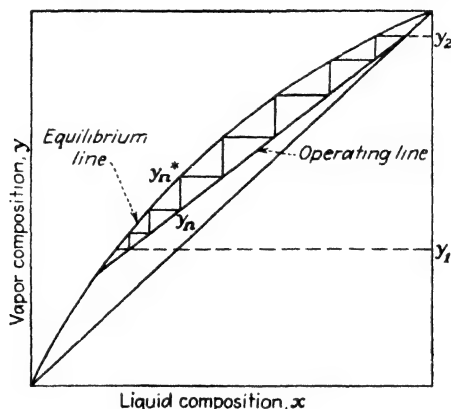
Fig. XIII.15.—Relation between the number of plates and the number of transfer units.

Between the terminal vapor compositions y_1 and y_2 there is a series of individual steps such as $y_n^* - y_n$, of varying spread in composition. Each of these corresponds to a theoretical plate. The transfer unit, on the other hand, corresponds to a step that is based on an average of the vertical distances $y_n^* - y_n$. It is clear that the number of units, or steps, may or may not be nearly the same in the two cases, depending on the relation between the operating and equilibrium lines. If these two lines were parallel, it is clear that the two numbers would be equal. This would be approximately true for an ideal solution of close-boiling components since in such a case the equilibrium line would never depart far from the diagonal.

Illustration 10.—Calculate (a) the number of transfer units and (b) the number of theoretical plates for the following cases:

1. Enrichment at total reflux of a 3.30 mole per cent liquid solution of *n*-heptane in methylcyclohexane to a product containing 96 per cent *n*-heptane. Assume ideal solution and $\alpha = 1.07$.

[1] Thomson, G. W., and H. A. Beatty, *Ind. Eng. Chem.*, **34**, 1124 (1942).

a. The equation applicable to this case is Eq. (13) in the paper by Dodge and Huffman,[1] *viz.,*

$$n = \frac{2.303}{\alpha - 1}\left(\log \frac{x_D}{x_F} + \alpha \log \frac{1 - x_F}{1 - x_D}\right)$$

Substituting $\alpha = 1.07$, $x_D = 0.960$, and $x_F = 0.033$,

$$n = 98$$

b. Equation (XIII.139) is applicable to this case.

$$E = \frac{96/4}{3.3/96.7} = 704$$

$$n = \frac{\log 704}{\log 1.07} = 98$$

The result is the same by either method, and for any system of this type the two concepts will give substantially the same number of units either at total reflux or at any finite reflux ratio.

2. Stripping a 5 mole per cent aqueous solution of a volatile component obeying Henry's law to a 0.01 per cent solution with a reflux ratio 1.20 times the minimum. Assume Henry's law constant = 3.0.

a. Equation (12) of the Dodge-Huffman paper is applicable, *viz.,*

$$n = \frac{2.303}{A} \log \frac{Ax_F + B}{Ax_n + B}$$

where
$$A = k - 1 - \frac{k}{R_E} \quad (k = \text{Henry's law constant})$$

$$B = \frac{x_W}{R_E}$$

$$R_E = \frac{F}{W}$$

By Eq. (XIII.111),

$$(R_E)_{\min} = \frac{kx_F - x_W}{(k - 1)x_F}$$

$$= \frac{3.00 \times 0.050 - 0.00010}{2.00 \times 0.050} = 1.50$$

$$(R_E)_{\text{actual}} = 1.20 \times 1.50 = 1.80$$

$$A = 2.00 - \frac{3.00}{1.80} = 0.333$$

$$B = \frac{0.00010}{1.80} = 0.0000556$$

$$n = 15.7$$

b. Applying Smoker's method to this case, one can readily derive

$$n = \frac{\log (x_F/x_W)}{\log (k/m)}$$

where m, the slope of the operating line $= R_E/(R_E - 1)$.

$$m = \frac{1.80}{0.80} = 2.25$$

$$n = \frac{\log (0.05/0.00010)}{\log (3.0/2.25)} = 21.6$$

[1] *Loc. cit.*

In this case there is an appreciable difference in the numbers of the two kinds of units, and the difference has no relation to the total number. Thus, by decreasing the reflux ratio the numbers can be made much larger, but they will not approach one another any more closely.

HEAT REQUIREMENT FOR DISTILLATION PROCESSES

Practically any continuous distillation process can be reduced for our present purpose to the over-all, or net, result indicated in Fig. XIII.16.
A feed that may be a liquid or a vapor or a mixture is split into two portions, a vapor V of composition y (in some specific cases, V will be condensed to a liquid, but it is immaterial to the present argument whether it is a liquid or a vapor), and a liquid residue of composition x. Q is the *net* heat transfer either to or from the surroundings, the former being reckoned as negative.

Fig. XIII.16.—General diagram of any continuous distillation process.

From the usual three balances, *i.e.*, total material, component A, and energy, one gets

$$F = V + L \tag{XIII.156}$$
$$Fz_F = Vy + Lx \tag{XIII.157}$$
$$FI_F = VH + Lh + (-Q) \tag{XIII.158}$$

Equation (XIII.158) can be put in a form symmetrical with the other two, as follows:

$$FI_F = VH' + Lh \tag{XIII.159}$$

where

$$H' = H - \frac{Q}{V}$$

or

$$q_V = H - H' \tag{XIII.160}$$

Elimination of all the masses[1] from Eqs. (XIII.156), (XIII.157), and (XIII.159) gives

$$\frac{z_F - x}{y - x} = \frac{I_F - h}{H' - h} \tag{XIII.161}$$

In general form, this is the same equation that has been obtained before in Chap. IX and earlier in this chapter [see Eq. (XIII.108)]. From the considerations discussed in Chap. IX it is well known that Eq. (XIII.161) can be represented on an enthalpy-concentration diagram as a straight line connecting the points whose coordinates are

$$(z_F, I_F), \ (x, h), \text{ and } (y, H')$$

and the net amount of heat per unit of vapor q_V is then obtained directly

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[1] The unit of mass is immaterial. Pounds can be used just as well as pound-moles.

in a very simple manner, as illustrated in Fig. XIII.17. The straight line is located by the two points h, x and I_F, z_F, and H' is then located by the intersection with the ordinate at y. H is located once the state of the vapor and its composition are known.

There is nothing special about basing the heat transfer on a unit mass of the vapor. Either of the other masses could have been chosen and exactly analogous relationships obtained.

For analytical determination of the heat-transfer requirement, Eq. (XIII.161) may be put in the form

$$q_V = (H - h) - \frac{y - x}{z_F - x} (I_F - h) \qquad \text{(XIII.162)}$$

The development of the graphical method of getting heat require-
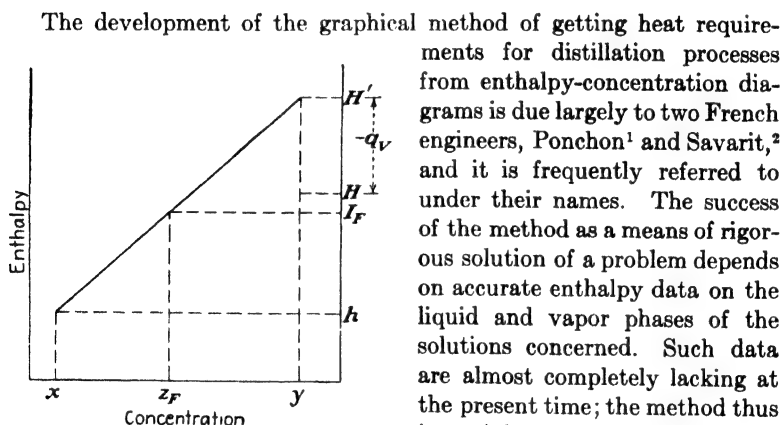
Fig. XIII.17.—General principle involved in getting heat requirements for distillation processes from an enthalpy-concentration diagram.

ments for distillation processes from enthalpy-concentration diagrams is due largely to two French engineers, Ponchon[1] and Savarit,[2] and it is frequently referred to under their names. The success of the method as a means of rigorous solution of a problem depends on accurate enthalpy data on the liquid and vapor phases of the solutions concerned. Such data are almost completely lacking at the present time; the method thus is mainly of academic interest. As a first approximation, one can assume ideal solutions, which makes the isotherms linear (see Chap. IX) and therefore requires a knowledge only of the properties of the two pure components. Any one of the special cases to be presently considered can be treated on this approximate diagram without very serious loss in accuracy.

In the following sections several special cases will be briefly discussed. For a more complete treatment of the application of enthalpy-concentration diagrams to problems in distillation and other related fields, the reader is referred to the book by Bošnjaković.[3]

[1] PONCHON, M., *Tech. Moderne*, **13**, 20 (1921).

[2] SAVARIT, R., *Arts et Metiers*, pp. 65, 142, 178, 241, 266, 307 (1922).

[3] BOŠNJAKOVIĆ, F. "Technische Thermodynamik," Vols. 1 and 2, T. Steinkopf, Leipzig, (1937).

Continuous Flash Distillation.—In the diagram in Fig. XIII.18, A represents the state of the feed that is taken to be a subcooled liquid, B is the state of the residual liquid, and C that of the vapor produced. The straight line that is at the basis of all constructions on such a diagram is BAD in this case. The heat per unit of vapor q_V is given directly by the diagram as shown, in accordance with Eq. (XIII.160).

Lines JI, BC, and EF are isotherms or equilibrium tie lines; they connect compositions of the two saturated phases that are in equilibrium. They are very useful for establishing the possible limits within which certain of the compositions may vary. Thus, for the given feed and
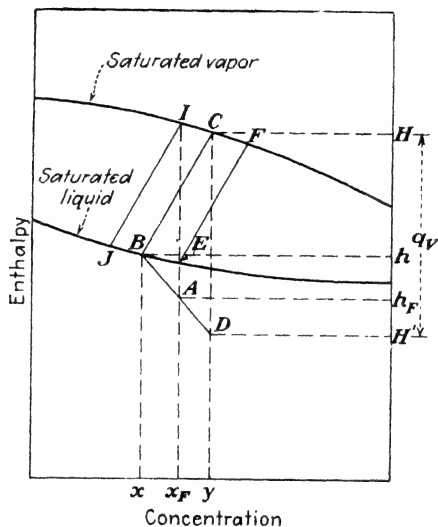
Fig. XIII.18.—Heat requirement for a continuous flash distillation.

residual liquid, the vapor composition must lie somewhere between the limits set by C and F, the former corresponding to equilibrium between vapor and residual liquid and the latter to equilibrium between vapor and feed. In a flash distillation it is usually assumed that the residual liquid and vapor are in equilibrium, and the construction in the figure is based on that assumption. If point C had been placed to the right of F, one could say at once that the process represented was an impossible one. The maximum possible limit of exhaustion of the less volatile component from the feed is given by point J since it denotes the state of the liquid in equilibrium with the totally vaporized feed.

Partial Integral Condensation.—The construction for this case is shown in Fig. XIII.19, where BAD is the fundamental straight line representing the equation

$$\frac{y_F - x}{y - x} = \frac{H_F - h}{H' - h} \qquad \text{(XIII.163)}$$

and
$$-q_V = H' - H \qquad \text{(XIII.164)}$$

Point I corresponds to the maximum possible concentration of volatile component in the condensate (total reflux), and hence G gives the maximum possible enrichment of the vapor. For a given feed vapor and residual vapor, there are two limiting cases for the composition of the condensate: (1) parallel current, with reflux liquid in equilibrium with residual vapor (point E); (2) countercurrent, with reflux in equilibrium with the feed (point F). It is evident by inspection of the diagram that,

Fig. XIII.19.—Partial integral condensation on an enthalpy-concentration diagram.

for a given vapor enrichment, the parallel-current condenser will require considerably more cooling water than the countercurrent condenser, since, for the latter case, point D would lie on the prolongation of line FA and, for the former case, on the prolongation of a line from E to A.

Differential Vaporization and Condensation.—The equation for vaporization may be derived directly from Eq. (XIII.162) by considering a differential amount of vapor, dV, formed in a small interval of time, and noting that the feed and residual liquid will differ only by an infinitesimal amount. These considerations at once transform Eq. (XIII.162) to

$$q_V = \frac{dQ}{dV} = (H - h) - (y - x)\frac{\partial h}{\partial x} \qquad \text{(XIII.165)}$$

The analogous equation for condensation, readily obtained by a similar

process, would be

$$-q_V = -\frac{dQ}{dV} = (H - h) - (y - x)\frac{\partial H}{\partial y} \qquad \text{(XIII.166)}$$

These equations have a very simple interpretation on the enthalpy-concentration diagram, which is illustrated for Eq. (XIII.165) in Fig.
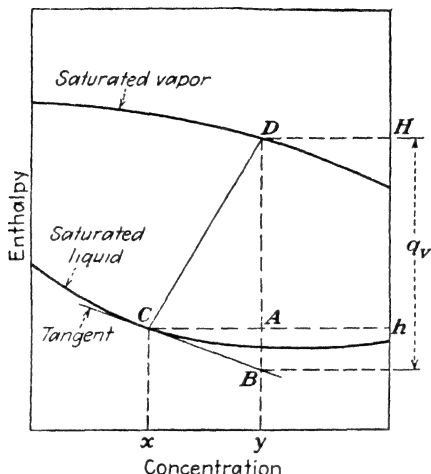
Fig. XIII.20.—Differential vaporization on an enthalpy-concentration diagram.

XIII.20.   The slope of the liquid line at C, dh/dx, equals the tangent of $\angle BCA$, or

$$\frac{dh}{dx} = -\frac{\overline{AB}}{y - x}$$

or

$$\overline{AB} = -(y - x)\frac{dh}{dx}$$

Comparing with Eq. (XIII.165), one sees at once that $dQ/dV = DB$ as shown in the figure.

The construction just illustrated gives only the instantaneous heat required for vaporization.   For a finite process an integration must be performed.

Since

$$dQ = q_V \, dV$$

and

$$dV = F d\zeta_V$$

$$Q = F \int_0^{\zeta_r} q_V \, d\zeta_V \qquad \text{(XIII.167)}$$

ζ_V is related to x by Eq. (XIII.28), and q_V is related to x as shown in Fig. XIII.20.   Having a series of corresponding values of ζ_V and q_V between the given limits, Eq. (XIII.167) can be evaluated graphically as the area under the curve of q_V vs. ζ_V.

This discussion is mainly of value as an illustration of principles rather than as a practical method of getting the heat requirement for a differential distillation process. The heat can probably be estimated with sufficient accuracy by assuming the process to be a flash distillation between the same limits of feed composition and at the same average composition of distillate.

Continuous Distillation Combined with Partial Condensation.—A diagrammatic representation of this process is shown in Fig. XIII.21. Liquid feed of composition x_F flows continuously into a still, and the bottom product of composition x_W is continuously withdrawn. The vapor is further separated by partial condensation into the overhead product of composition y_D and into a reflux of composition x_0. By such a process it is possible to produce substantially pure component A as head product if the condensation is a differential one, but the limiting value of x_W is that of a liquid in equilibrium with a vapor of composition $y_F = x_F$ (see Fig. XIII.22).

The usual three balances over the entire system lead to the equation

$$\frac{x_F - x_W}{y_D - x_F} = \frac{h_F - h_W}{H' - h_F} \qquad \text{(XIII.168)}$$

where

$$H' = H_D + q_C - q_D \qquad \text{(XIII.169)}$$

and

$$q_C = \frac{Q_C}{D}$$

$$q_D = \frac{Q_B}{D}$$

Equation (XIII.168) represents a straight line on the enthalpy-composition diagram connecting the points (x_F, h_F), (x_W, h_W), and (y_D, H'). Similarly, the same balances on the condenser alone lead to a straight line between the points (y_V, H_V), (x_0, h_0), and (y_D, H'') where

$$H'' = H_D + q_C \qquad \text{(XIII.170)}$$

From Eqs. (XIII.169) and (XIII.170),

$$q_D = H'' - H' \qquad \text{(XIII.171)}$$

The graphical construction for getting q_D is shown in Fig. XIII.22. ABC and DEF are the two straight lines that are the key lines of the construction. y_V is assumed to be in phase equilibrium with x_W, which may have any value between x_F and the composition corresponding to G. The upper limit to the value of x_0 is y_V since that would call for total condensation. The diagram shows at once that the heat requirement would approach infinity at this limit because the line DEF would be vertical. It is also evident by inspection that an increase in purity of the head product increases the heat demand.
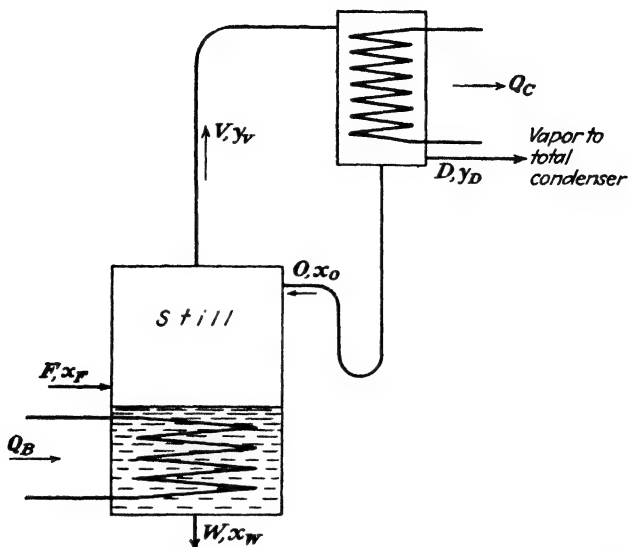
FIG. XIII.21.—Continuous distillation combined with partial condensation.
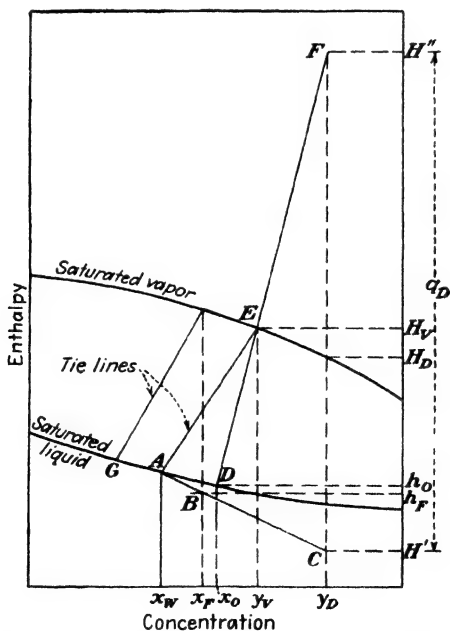
FIG. XIII.22.—Heat requirements for continuous distillation combined with partial condensation.

Rectification.—From Eq. (XIII.88) it can be seen that any operating line in the rectifying section of a column is a straight line on the enthalpy-concentration diagram passing through the points (x_D, h'_D), (y, H), and (x, h). All the operating lines for this section of the column (ABC in Fig. XIII.23 is one such line) will pass through the point C whose location depends on the reflux ratio and hence on the amount of heat removed in the condenser, as is evident from Eq. (XIII.84). The heat q_C taken out in the condenser per unit amount of distillate is readily obtained from the figure as shown.

Fig. XIII.23.—Rectification illustrated on an enthalpy-concentration diagram.

Since an equilibrium tie line or isotherm (two examples are shown at JK and FG, Fig. XIII.23) represents the maximum spread that can occur between vapor and liquid phases in contact, the operating lines must always have a greater slope than the tie lines between the same points. When the operating lines are vertical ($y = x$), it is immediately evident from the diagram that q_C will be infinite and we have the case of total reflux. When the operating lines coincide with the tie lines, they will have the least possible slope and hence will intersect the x_D ordinate at the lowest possible point, which means the least heat out in the condenser. This is the case of minimum reflux. Since the tie lines have different slopes, they will cut the product-composition ordinate at different points and the minimum reflux for the section will correspond to the highest point. In other words, the minimum reflux is a maximum of minima,

as previously pointed out. This point is illustrated in **Fig. XIII.24,** which shows three positions of point C corresponding to the intersections of three straight lines that coincide with the isotherms. The minimum reflux is determined by C'', where the heat to be removed, and hence the reflux, is a maximum of the three minima.

From Eqs. (XIII.84) and (XIII.88) one obtains

$$(q_C)_{\min} = H - h_D + (H - h) \frac{x_D - y^*}{y^* - x} \qquad \text{(XIII.172)}$$

when the operating line for any level coincides with the isotherm on the
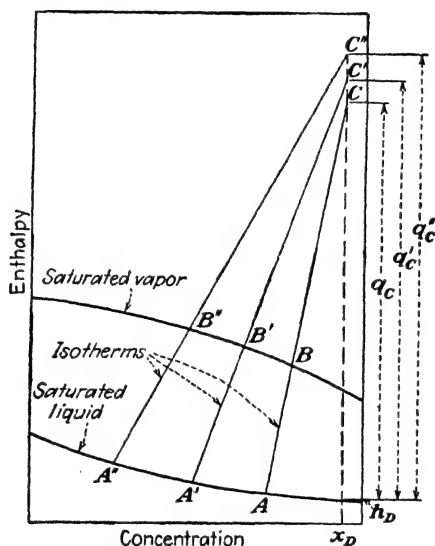
Fig. XIII.24.—Minimum reflux.

Hx diagram. In the great majority of cases the minimum is governed by the feed level and Eq. (XIII.172) becomes

$$(q_C)_{\min} = H_F - h_D + (H_F - h_F) \frac{x_D - y_F^*}{y_F^* - x_F} \qquad \text{(XIII.173)}$$

Equation (XIII.108) shows that a straight line connects point C, the feed-state point N, and a point M (see Fig. XIII.23) whose coordinates are (x_W, h_W'). Equation (XIII.99) shows that all the operating lines of the exhausting column pass through this latter point, and hence it is an axis for these lines exactly analogous to C for the rectifying section. Note that the point M is fixed by the feed state and the location of C.

q_B, the heat required in the boiler per unit of bottom product, is obtained as shown in Fig. XIII.23 on the basis of Eq. (XIII.100).

From Eqs. (XIII.102) to (XIII.104) one can derive

$$\frac{x_W - z_F}{z_F - x_D} = \frac{h_W - I_F}{I_F - h_D''} \tag{XIII.174}$$

where

$$h_D'' = h_D + q_C - q_D \tag{XIII.175}$$

and

$$q_D = \frac{Q_B}{D}$$

The graphical construction based on these equations to obtain the heat requirement q_D for the boiler per unit of distillate is shown in Fig. XIII.25.
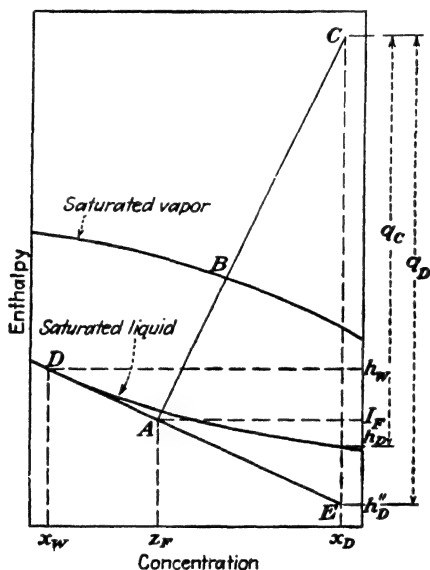
FIG. XIII.25.—Heat requirement for rectification.

DAE is the straight line representing Eq. (XIII.174), and ABC is an operating line for the rectifying section whose location depends on a knowledge of q_C, the heat to be removed in the condenser, which is, of course, related to the reflux ratio.

The minimum heat requirement would correspond to the minimum reflux ratio, which in turn is determined by the lowest possible location for the axis C. The following algebraic relation for calculation of minimum q_D is readily obtained from Eqs. (XIII.173) to (XIII.175):

$$(q_D)_{\text{min}} = H + (H - h)\frac{x_D - y^*}{y^* - x} - I_F - (I_F - h_W)\frac{x_D - z_F}{z_F - x_W} \tag{XIII.176}$$

Unless it were known that the feed level required the maximum of the various possible minima, the solution must be by trial, or the graphical method must be used.

If the boundary lines for the saturated phases were horizontal straight lines, which would be the case for constant molal overflow since this assumes equal latent heats, no heat of mixing, and equal sensible heats of the liquids, it is clear from the diagram of Fig. XIII.25 that the heat required in the boiler would equal that to be taken out in the condenser ($q_C = q_D$) if the feed were liquid at the boiling point. In all other cases, these two heats would not, in general, be equal.

To produce either pure component B in a differential distillation or pure A in a combination of distillation with a reflux condenser would require, at the limit, an infinite amount of heat; but, by the process of rectification, complete separation into the two pure components is theoretically possible with a finite amount of heat. This can be seen from Fig. XIII.25, where it is evident that, at the limit where $x_D = 1$, q_D would still be a finite quantity.

Determination of Number of Plates.—Although the determination of the number of plates is somewhat out of place in a discussion of heat requirements, it is inserted here because, while on the subject of enthalpy-concentration diagrams, it is of interest to show how this can be done by a stepwise procedure on such a diagram if the equilibrium yx curve is also available to permit the location of the tie lines at any point. In Fig. XIII.23, point F represents the state of the vapor leaving the top plate of the column for the case where a total condenser is used to produce the reflux. By following a tie line, point G is reached which corresponds to the composition of the liquid on the top plate if it were a theoretical one as previously defined. A straight line from G to C is an operating line, and hence J must represent the state of the vapor rising from the plate below. By continuing this zigzag procedure along alternate tie and operating lines until the feed level is reached, one gets the number of plates for the rectifying section. The number of plates for the exhausting section is obtained in an entirely analogous manner, but with operating lines passing through the axis M.

There is little point in using the enthalpy-concentration diagram to determine the number of plates because the use of the yx diagram is simpler and just as general if one does not make the usual simplifying assumptions. As a matter of fact, the difference between the result obtained from an Hx diagram and that from the usual yx diagram with linear operating lines (McCabe-Thiele method) is generally small and of little practical importance, especially when one bears in mind that differences in equilibrium data are often of greater importance in affecting the result.

It is to be concluded that the chief use of the enthalpy-concentration diagram in distillation is to determine heat quantities or to aid in visualizing the effects of certain changes and not for calculation of number of

plates. The main obstacle at the present time to any practical use of these diagrams, even for heat quantities, is that there are so few data available for their construction.

Effect of Heat Loss.—Up to this point we have considered the column to be adiabatic, but it is also of interest to consider the effect of a heat loss from the column. Let q_R and q_E be the heat lost to the surroundings from the enriching and exhausting sections per unit of head and bottom
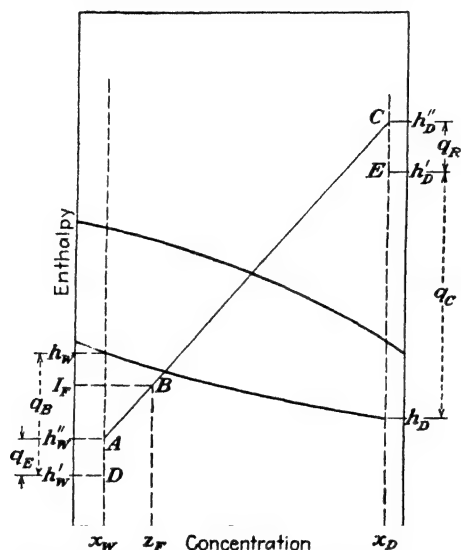
Fig. XIII.26.—Effect of heat loss from a column.

products, respectively. The heat-balance equation for the whole column becomes

$$FI_F = Dh''_D + Wh''_W \tag{XIII.177}$$

where

$$h''_D = h_D + q_C + q_R \tag{XIII.178}$$

$$h''_W = h_W - q_B + q_E \tag{XIII.179}$$

In Fig. XIII.26, ABC is the straight line representing Eq. (XIII.177); the various heat quantities are also indicated. Considering a level above the top plate of the column, $q_R = 0$ above this level, and the axis of the operating lines is E. As one moves down in the column, q_R increases until the feed level is reached where q_R reaches its total value and the operating-line axis is C. In other words, the operating-line axis shifts from E to C as one proceeds down the column. From Fig. XIII.23 it is evident that, the higher the axis, the smaller the number of plates required; hence, a fixed axis at C calls for less plates than does the case where the axis varies from C to E. From this it can be concluded that for the same

total amount of reflux or the same total heat removal in the combined condenser and enriching section, an adiabatic column requires less plates than one with heat loss. Putting it in another way, it is better to remove the total heat $q_R + q_D$ in the condenser than part in the condenser and the rest in the column.

Similar reasoning applies to the exhausting column, where the operating-line axis moves from D to A as the balance level is moved from the bottom to the feed level. Operating-line axis D calls for the least number of plates, and this would be the fixed axis of an adiabatic column using the same heat input q_B as the nonadiabatic one. One may therefore conclude that an adiabatic exhausting column requires less plates (or gives better separation for the same number of plates) than a nonadiabatic one with the same heat input.

Similar conclusions can be reached in the case of columns operating below the temperature level of the surroundings. In this case the heat flow is a heat leak in.

It is of some interest to note that, if a nonadiabatic column in which heat q_C is removed by the condenser and q_R is lost from the enriching section is subsequently lagged to render the loss negligible, without at the same time providing for any increase in q_C, the axis becomes fixed at E and the separation will consequently be poorer than it was in the unlagged column. To gain an advantage from lagging, the cooling effect in the partial condenser must be increased; or if a total condenser is used, the reflux ratio must be increased.

Approximate Methods for Heat Requirement.—The methods based on the use of the enthalpy-concentration diagram are elegant and at the same time simple provided that the diagram is available. The data for constructing such diagrams are generally lacking; even if they were available, the labor of making the diagram would not be warranted when only a few calculations are to be made. By assuming linear enthalpy-concentration lines for the two saturated phases the diagram is enormously simplified since we then need thermal data only on the pure components. Assuming constant average specific heats,

$$h_A \text{ (molal)} = C_{p_A} M_A (t_A - t_0) \qquad (\text{XIII.180})$$

where t_0 is the datum temperature. If t_A is the boiling point of A, then one gets the value of h_A on the saturated-liquid line.

For the saturated vapor, $\qquad H_A = h_A + L_A \qquad (\text{XIII.181})$

with similar equations for the other component. Using these equations to locate the boundary lines for the two phases, the heat q_D can then be found from the graphical construction previously outlined or by Eq. (XIII.176).

If the liquids are similar, one may be justified in going one step further and assuming

$$h_A = h_B = h$$
$$L_A = L_B = L^*$$
$$\therefore H_A = H_B = H$$

Substitution in Eq. (XIII.176) coupled with Eq. (XIII.86) results in the equation

$$q_D = L_m(R + 1) \qquad \text{(XIII.182)}$$

for the case where the feed is a liquid substantially at the boiling point. The equation is the same in form regardless of whether R is the minimum reflux ratio or any value greater than minimum.   If the feed is not at the boiling point, a term to take care of preheating the feed can easily be added if necessary.

It is very doubtful if the use of an actual enthalpy-concentration diagram is justified for any but a few very special cases.   For example, even in the case of acetic acid–water mixtures where the difference in latent heats is unusually great, the difference between using an enthalpy-concentration diagram with linear saturation lines and using Eq. (XIII.182) is rather small and within the accuracy needed in most heat calculations, as the following illustration shows.

Illustration 11.—A 50 mole per cent solution of acetic acid in water is to be rectified at atmospheric pressure in a continuous column to produce an overhead product containing only 0.5 mole per cent HAc and a bottom product of 99.0 mole per cent acid.   Assume the feed enters substantially at the boiling point, which is 104°C. Estimate the minimum amount of heat needed in the boiler per mole of head product.

The following data will be used:

C_p of HAc $= 0.522$ c.h.u./lb./°C.   ("Chemical Engineers' Handbook")
(assumed constant over the range considered)
L of HAc $= 97.0$ c.h.u./lb. at normal boiling point (118°C.) (International Critical
Tables) $= 5,820$ c.h.u./mole
L of water $= 9,700$ c.h.u./mole at 1 atm.

Vapor in equilibrium with 50 mole per cent solution contains 62.7 mole per cent H_2O.[†]   All values of enthalpy will be given in centigrade heat units per pound-mole above a datum level of 80°C.

$$h_A \ (A \text{ for water}) = 18 \times 20 = 360$$
$$h_B = 60 \times 0.522 \times (118 - 80) = 1,190$$
$$H_A = 360 + 9,700 = 10,060$$
$$H_B = 1,190 + 5,820 = 7,010$$

From Fig. XIII.27 based on the construction illustrated in Fig. XIII.25, q_D (heat required in boiler per mole of overhead product) $= 32,000$ c.h.u.   This assumes

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* In an actual case the latent heats would not be equal, and it is suggested that an arithmetic mean be used.

† CORNELL, L. W., and R. E. MONTONNA, *Ind. Eng. Chem.*, **25**, 1331 (1933).

that the minimum heat requirement is determined by equilibrium at the feed level, and hence the operating line in the diagram coincides with the tie line for the feed
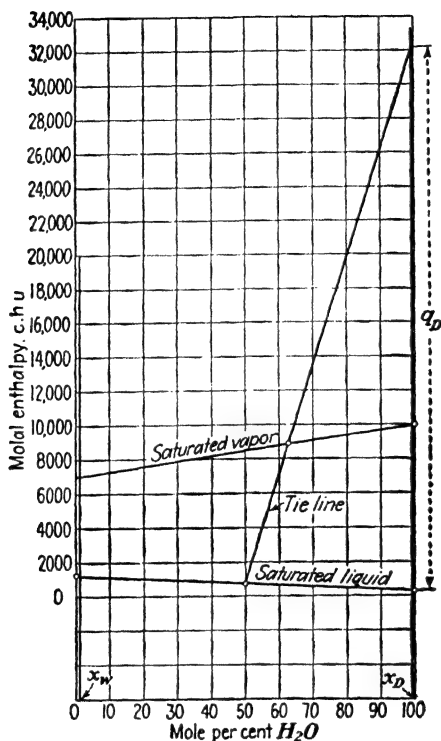
FIG. XIII.27.—Diagram for the solution of Illustration 11.

level.   The same calculation may be made analytically from Eq. (XIII.176), where the various quantities have the following values (assuming linear saturation lines):

$$H = H_F = H_A y_F + H_B(1 - y_F)$$
$$= 10,060(0.627) + 7,010(0.373) = 8,940$$
$$h = h_F = h_A x_F + h_B(1 - x_F)$$
$$= 775$$
$$h_W = 368$$
$$I_F = h_F$$
$$z_F = x_F = 0.500$$

From Eq. (XIII.176), $q_D = 31,500$

From Eq. (XIII.182), $q_D = L_m(R + 1)$

$$R_{(min)} = \frac{x_D - y_F^*}{y_F^* - x_F}$$

$$q_D = \left(\frac{9,700 + 5,820}{2}\right)\left(\frac{0.995 - 0.627}{0.627 - 0.500} + 1\right) = 30,300$$

The difference between the two methods is only about 5 per cent. Of course, it is recognized that an assumption was made about the course of the saturation lines, but it is believed that the use of the correct lines would not change the conclusion very much.

Efficiency of a Rectifying Column.—Earlier in this chapter, methods were given for calculating the minimum theoretical work or heat requirement for separation of solutions. With such a figure as a standard, we are able to investigate the efficiency of any of the distillation processes that have been discussed. By way of illustration, the thermodynamic efficiency of the process of rectification in the usual adiabatic column will be calculated.

Illustration 12.—What is the thermodynamic efficiency of a rectification process for carrying out the complete separation of Illustration 1, using steam at 50 lb. absolute pressure?

$$R_{(min)} = \frac{1.00 - 0.715}{0.715 - 0.500} = 1.33$$

$$L_m = 7,650 \times 1.8 = 13,800 \text{ B.t.u./lb.-mole}$$

By Eq. (XIII.182), $q_D = 13,800(1 + 1.33) = 32,000$ B.t.u./lb.-mole of head product

Assuming the condensate from the steam to be removed at the saturation temperature,

$$\text{Steam requirement} = \frac{32,000}{924} = 34.6 \text{ lb.}$$

$$\text{Thermodynamic efficiency} = \frac{4.98^*}{34.6} \times 100 = 14.4 \text{ per cent}$$

From this illustration one can conclude that a rectifying column is a very inefficient instrument from a thermodynamic standpoint. Most actual columns will, of course, be much less efficient than this owing to the necessity of using considerably more than the minimum reflux. There are several places where irreversible effects occur in an ordinary adiabatic rectifying column such as (1) temperature differences in the boiler and condenser, (2) pressure drop due to fluid flow, and (3) transfer of material between phases not at phase equilibrium. These irreversibilities and their effect on the thermodynamic efficiency of a column were briefly considered in Chap. X.

Reduction of Heat Requirement.—In the case of difficult separations the heat requirement may be so great that the steam cost is a serious item of expense. One possible means of reducing the steam consumption is to utilize the multiple-effect principle, which has been common practice for a long time in the unit operation of evaporation. This would require a series of stills, each one operating at a lower pressure and temperature than the preceding one so that the vapor from a given still could be condensed in the heating coils of the boiler of the succeeding one. Steam

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* See Illustration 1 for this minimum thermodynamic requirement.

would be fed only to the boiler of the first, or highest-pressure, still. The principle is sound; but the possible gain in economy has evidently not been sufficient in most cases to justify the increase in first cost of such a system and the greater operating difficulties, since very few installations involving the multiple-effect principle have been put into operation as far as the author is aware. The use of this general principle was
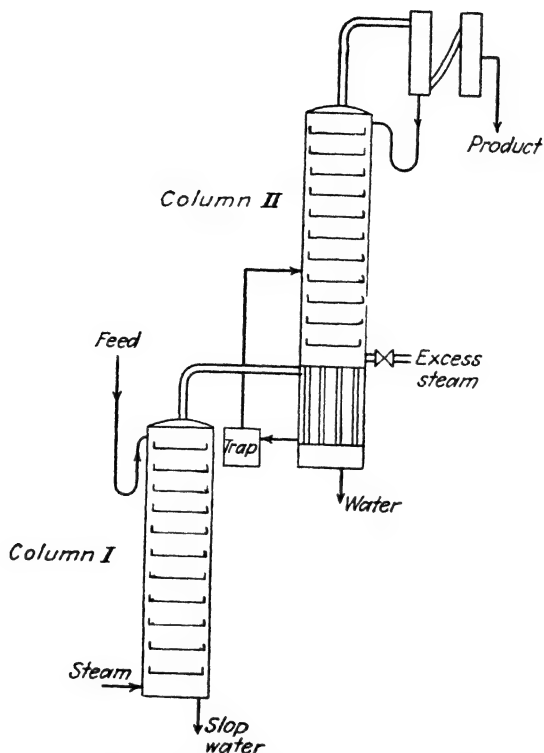
Fɪɢ. XIII.28.—Vulcan vapor reuse process.

proposed by Calingaert[1] in 1925; but one objection to his process is that the reflux is produced in a partial condenser, and hence only the product vapor is used as a heating medium. In any difficult separation, most of the heat would be taken out in the reflux condenser. It would seem as if little gain in economy could be effected this way. From the standpoint of principle, it would appear to be better to condense totally all the vapor in the boiler of the next effect and then divide the condensate into reflux and product.

[1] Cᴀʟɪɴɢᴀᴇʀᴛ, G., *Chem. Met. Eng.*, **32**, 362 (1925).

A vapor re-use scheme that is claimed to overcome some of the practical difficulties of a multiple-effect system was proposed by Othmer.[1] One possible application of the idea is indicated in Fig. XIII.28.   Column I is an exhausting column that operates at an elevated pressure (of the order of 50 lb. per sq. in.) with live steam.   The vapor from the top of the column is condensed in the tubes of the boiler of column II, which operates at substantially atmospheric pressure, and this condensate is introduced into II as its feed liquor.   Column II makes a complete separation of the feed into the two substantially pure components and
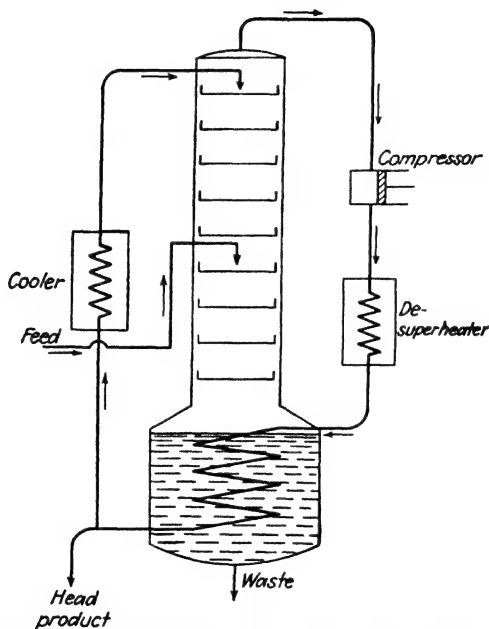
FIG. XIII.29.—Rectification process using vapor recompression.

requires no steam.   In fact, in the illustration given by Othmer, *viz.*, the rectification of a 2.5 per cent solution of acetone in water, the second column is said to produce an excess of steam that may be drawn off and used elsewhere.

Another means of saving heat is to utilize a heat pump or vapor-recompression system as shown diagrammatically in Fig. XIII.29. In such a system the boiler and condenser (which must be a total one, producing both reflux and head product) are combined in a single unit, and the energy for the distillation is supplied as work rather than as heat.   For any given case the work input to the compressor is a fixed

[1] OTHMER, D. F., *Ind. Eng. Chem.*, **28**, 1435 (1936).

amount, and this must be balanced by the difference in enthalpies of the various fluid streams entering or leaving the system, plus any heat taken out in the cooler and desuperheater or lost by radiation. It is clear that these various energy quantities will not automatically balance; some adjustment must be made. If the work is too great, some of the vapor can be by-passed to a condenser instead of going to the compressor; if too small, auxiliary heating by steam can be used.

From the principle of the heat pump as discussed in Chap. X on Refrigeration it is clear that the amount of work depends on the temperature difference against which the heat must be pumped. In the case of separation of ethyl alcohol–water solutions, for example, the minimum possible difference is about 40°F.; another 15 to 20° must be added to this to allow a reasonable rate of heat transfer in the boiler. As the following illustration shows, this is not a very favorable case for application of this principle.

Illustration 13.—Make an approximate comparison of the cost of power for the vapor-recompression process of Fig. XIII.29 with the cost of steam for an ordinary rectification column, to separate a 20 mole per cent ethyl alcohol–water solution into a head product containing 86.0 mole per cent EtOH and a bottom product that is substantially pure water.

Assume that the heat requirement is to be a minimum for the given separation or that the column is to operate with minimum reflux.

By Eq. (XIII.86), assuming constant molal reflux,

$$R_{\min} = \frac{y_D - y^*}{y^* - x}$$

Because of the abnormal shape of the equilibrium curve for this system, the minimum reflux does not correspond to equilibrium at the feed level, as the following tabulation shows:

x	y^*	$R_{\min}$
0.2000	0.5285	1.01
0.5000	0.652	1.37
0.7600	0.7905	2.28
0.7800	0.8040	2.33
0.7900	0.8108	2.36
0.8000	0.8175	2.43
0.8100	0.8248	2.38
0.8200	0.8320	2.33

The equilibrium data are those of Lewis and Carey.[1] The minimum R will be taken to be 2.43. By Eq. (XIII.182),

$$q_D = 17,200(2.43 + 1) = 59,000 \text{ B.t.u./lb.-mole of head product}$$

[1] Lewis, W. K., and J. S. Carey, *Ind. Eng. Chem.*, **24**, 882 (1932).

17,200 is the average of the molal latent heats of vaporization of ethyl alcohol and water at 1 atm

In the calculation of the work of compression, assume the product vapor is an ideal gas, that k (ratio of specific heats) $= 1.16$, and that a 10°C. temperature difference is to be available for heat transfer in the boiler. This means that the alcohol vapor is to be condensed at 110°C., where its vapor pressure is 3.11 atm.

By Fig. VII.8,

$$\text{Theoretical work of compression per lb.-mole of vapor} = 0.500 \times \frac{460 + 176}{530}$$
$$\times 0.746 = 0.449 \text{ kw.-hr.}$$

Assuming 70 per cent efficiency and compression of all the vapor from the column,

$$\text{Work} = \frac{0.449}{0.70} \times 3.43 = 2.20 \text{ kw.-hr.}$$

Assuming exhaust steam at 10 lb. gauge costs 30 cents per 1,000,000 B.t.u. and electrical energy costs 1 cent per kw.-hr., the cost of the steam would be

$$\frac{59,000}{10^6} \times 30 = 1.77 \text{ cents}$$

against 2.20 cents for the power. The compression system would save some cooling water; but a considerably larger heating surface would be required in the boiler since the Δt in the case of steam heating would be 28°F. as compared with 18°F. for vapor heating, and the transfer coefficient would also be greater in the former case.

Vapor recompression would be attractive only where electrical energy is very cheap or where the temperature difference over which the heat must be pumped is considerably smaller than in the illustration.

Space does not permit us to make an analyis of other vapor re-use systems to compare their economy with that of an ordinary rectification. This is suggested as an interesting comprehensive problem for the student.

APPENDIX

TABLE I.—PRESSURE EQUIVALENTS[1]

Bars or megadynes/sq. cm.	kg./cm.²	lb./sq. in.	Short tons/sq. ft.	atm.	Columns of Hg at 0°C.		Columns of H₂O at 15°C.			lb./sq. ft.	kg./m.²	mm. of Hg
					m.	in.	m.	in.	ft.			
1	1.0197	14.50	1.044	0.9869	0.7500	29.53	10.21	401.8	33.48	2,088	10,197	750.044
0.9807	1.	14.22	1.024	0.9678	0.7355	28.96	10.01	394.0	32.84	2,047.17	10,000	735.514
0.06895	0.07031	1	0.072	0.06804	0.05171	2.036	0.7037	27.70	2.309	144	703.1	51.710
0.9576	0.9765	13.89	1	0.9450	0.7182	28.28	9.773	384.8	32.06	2,000.16	9,765	718.20
1.0133	1.0333	14.70	1.058	1	0.76	29.92	10.34	407.2	33.93	2,116.8	10,333	760
1.3333	1.3596	19.34	1.392	1.316	1	39.37	13.61	535.7	44.64	2,784.96	13,596	1,000
0.03386	0.03453	0.4912	0.03536	0.03342	0.02540	1	0.3456	13.61	1.134	70.733	345.3	25.399
0.09798	0.09991	1.421	0.1023	0.09670	0.07349	2.893	1	39.37	3.281	204.624	999.1	73.492
0.002489	0.002538	0.03610	0.002599	0.0024560	0.001867	0.07349	0.02540	1	0.08333	5.1984	25.38	1.867
0.02986	0.03045	0.4332	0.03119	0.02947	0.02240	0.8819	0.3048	12	1	62.3808	304.5	22.40

1 g./sq. cm. = 980.597 dynes/sq. cm. = 0.45762 poundal/sq. in.
1 dyne/sq. cm. = 0.001019716 g./sq. cm. = 0.000466642 poundal/sq. in.
1 poundal/sq. in. = 2142.97 dynes/sq. cm. = 2.18536 g./sq. cm. = 0.031081 lb./sq. in.

[1] From J. H. PERRY, "Chemical Engineers' Handbook," 2d ed., p. 105, McGraw-Hill Book Company, Inc., New York, 1941.

TABLE II.—ENERGY CONVERSION FACTORS[1]

Joules = 10^7 ergs	kg.-m.	ft.-lb.	kw.-hr.	hp.-hr.	liter-atm.	kg.-cal.	B.t.u.	g.-cal.
1	0.10197	0.7376	$0.0_4 2778$	$0.0_6 3725$	0.009869	$0.0_3 2390$	$0.0_3 9486$	0.239
9.80597	1	7.233	$0.0_5 2724$	$0.0_5 3653$	0.09678	0.002344	0.009296	2.3438
1.356	0.1383	1	$0.0_6 3766$	$0.0_6 50505$	0.01338	$0.0_3 3241$	0.001286	0.3241
3.6×10^6	3.671×10^5	2.655×10^6	1	1.341	35,528	859.98	3,415	860,445
2.6845×10^6	2.7375×10^5	1.98×10^6	0.7457	1	26,494	641.7	2,545	641,659
101.33	10.333	74.73	$0.0_4 2815$	$0.0_4 3774$	1	0.02422	0.09612	24.218
4,183	426.9	8,086	0.001162	0.001558	41.29	1	3.968	999.936
1,054	107.5	778.1	$0.0_3 2928$	$0.0_3 3930$	10.40	0.25200	1	252

1 therm = 100,000 B.t.u.

[1] From J. H. Perry, "Chemical Engineers' Handbook," 2d ed., p. 104, McGraw-Hill Book Company, Inc., New York, 1941.

TABLE III.—VALUES OF GAS CONSTANT R IN VARIOUS UNITS

Units	R
Atm., cc. per g.-mole, °K	82.06
Atm., liters per g.-mole, °K	0.08206
C.h.u. per lb.-mole, °K	1.987
B.t.u. per lb.-mole, °R	1.987
Lb. per sq. in. abs., cu. ft. per lb.-mole, °R	10.73
Lbs. per sq. ft. abs., cu. ft. per lb.-mole, °R	1544
Atm., cu. ft. per lb.-mole, °R	0.730
Kw.-hr. per lb.-mole, °K	0.001049
Hp.-hr. per lb.-mole, °R	0.000780
Atm., cu. ft. per lb.-mole, °K	1.3145
Mm. Hg, liters per g.-mole, °K	62.37
In. Hg, cu. ft. per lb.-mole, °R	21.85

TABLE IV.—CRITICAL CONSTANTS AND CONSTANTS a AND b OF VAN DER WAALS'
EQUATION*
(Units of a and b: atm., cu. ft., °K., and lb.-moles)

Substance	T, °K.	p, atm.	Critical volume, cu. ft./ lb.-mole	$\dfrac{p_c v_c}{RT_c}$	Van der Waals constants†	
					a	b
Acetylene..................	309.1	61.7	1.81	0.2755	1,129.	0.8232
Air.......................	132.4	37.2	1.32‡ 1.49§	0.284 0.321	343.5	0.585
Allylene..................	401.					
Ammonia.......... . ..	405.5	111.5	1.16	0.2425	1,076.	0.598
Argon............	151.	48.	1.21	0.293	346	0.517
Benzene.......... .	561.6	47.7	4.11		4,820.	1.935
Boron trifluoride.... .	260.8	49.2			1,009.	0.871
n-Butane........... .	426.0	36.0	4.01		3,675.	1.944
Carbon dioxide..	304.1	72.9	1.54	0.280	925.	0.686
Carbon monoxide . .	134.4	34.6	1.44	0.282	381.	0.639
Carbon oxysulfide. . .	378	61.			1,708.	1.02
Chlorine..	417.	76.	1.99	0.275	1,668.	0.90
Cyanogen	401.	59.			1,544.	1.12
Cyclohexane............ ..	554.1	40.6	4.95		5,513.	2.242
Dichlorodifluoromethane....	384.6	39.56	3.55	0.276	2,726.	1.595
Dichloromethane...........	489.	51.4			3,392.	1.564
Diethyl amine.............	496.4	36.58			4,923.	2.229
Difluorotetrachloroethane....	551.1					
Diisobutyl...............	549.9	24.5	7.72		8,997.	3.688
Diisopropyl	500.5	30.6	5.72		5,966.	2.688
Dimethyl amine..	437.7	52.4			2,665.	1.372
Ethane	305.2	48.8	2.20	0.279	1,391.	1.028
Ethyl chloride...	460.3	52.			2,970.	1.455
Ethylene..... ..	282.8	50.7	2.14	0.33	1,150.	0.9165
Fluorine... . .	144.	55.			302.7	0.418
Helium.....	5.2	2.3	0.97	0.328	8.57	0.372
n-Heptane	540.0	26.8	6.84		7,931.	3.311
n-Hexane..........	507.9	29.5	5.88		6,374.	2.829
Hydrocyanic acid.	458.6	56.9	2.22	0.209	2,693.	1.323
Hydrogen........	33.2	12.8	1.03	0.306	62.8	0.426
Hydrogen bromide...	363.	84.			1,144.	0.71
Hydrogen chloride....	324.5	81.6			942.	0.654
Hydrogen iodide.....	424.	82.			1,598.	0.85
Hydrogen sulphide.	373.5	88.9			1,145.	0.691
Isobutane.............	407.1	37.0	3.99		3,265.	1.808
Isopentane............. .	460.9	32.92	4.93		4,704.	2.300
Krypton................	210 ?	54. ?	1.70 ?		596. ?	0.64 ?
Mercury................	1,172.	180.			5,100.	1.070
Methane................. .	191.1	45.8	1.59	0.289	581.2	0.6855
Methyl chloride.....	416.2	65.8	2.19 ?		1,920.	1.041
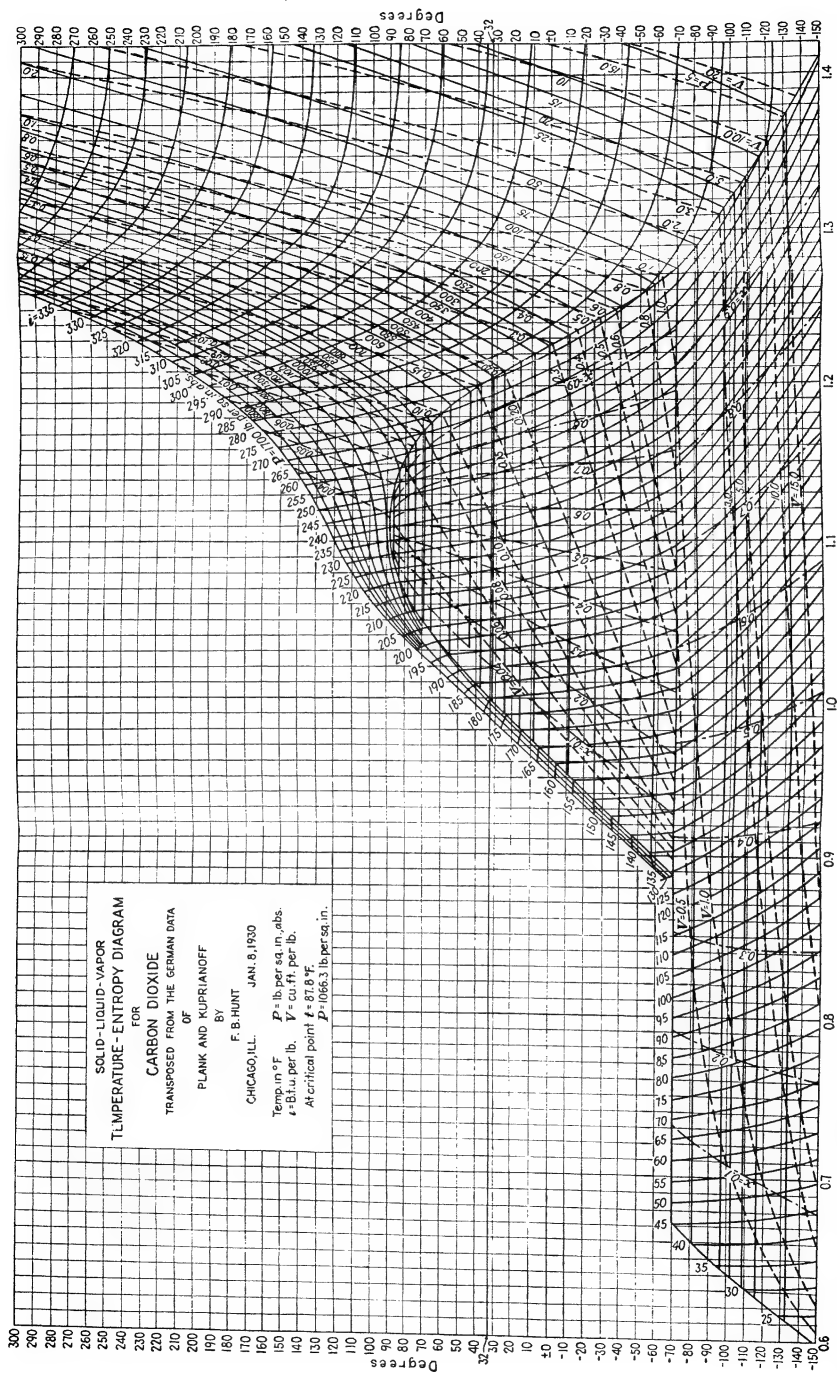
Solid-liquid-vapor-temperature-entropy diagram for carbon dioxide. Note that i is used for enthalpy in B.t.u. per pound. (Courtesy of F. B. Hunt of the Liquid Carbonic Corporation. The data of Plank and Kuprianoff are published in Z. ges. Kälte-Ind., Beih/16, **1**, 10-65 (1929).

(Facing page 662)

TABLE IV.—CRITICAL CONSTANTS AND CONSTANTS a AND b OF VAN DER WAALS' EQUATION.*—(*Continued*)

Substance	T, °K.	p, atm.	Critical volume, cu. ft./ lb.-mole	$\dfrac{p_c v_c}{RT_c}$	Van der Waals constants†	
					a	b
Methyl fluoride............	317.6	58.0			1,268.	0.899
Monoethyl amine.......... .	456.3	55.54			2,735.	1.351
Monomethyl amine..	430.0	73.6			1,832.	0.960
Monopropyl amine.	496.9	46.76			3,853.	1.747
Neon................... ..	44.4	25.9	0.66	0.297	55.4	0.282
Nitric oxide...............	179. ?	65. ?			359.	0.45 ?
∨ Nitrogen.................	126.0	33.5	1.44	0.292	346.	0.618
Nitrous oxide..............	309.6	71.7	1.57 ?		974.	0.709
n-Octane.............. ...	569.3	24.6	7.85		9,604	3.803
Oxygen..................	154.3	49.7	1.19	0.292	349.5	0.510
Ozone.................	268. ?	92. ?			569.	0.479
n-Pentane......	470.3	33.0	4.98		4,886.	2.342
Phosgene........	456. ?					
Phosphine.....	325.	65.			1,185.	0.82
Phosphorus..... ...	948 1	80.			8,200.	1.945
Propane	369 9	42.01	3.12		2,374.	1.446
Propyl chloride.. .	503.2	45 18			4,187.	1.828
Propylene.......... ..	364.8	45.0	2.91		2,155.	1.332
Silicon tetrafluoride	272.	50.			1,079.	0.89
Sulphur dioxide..... . ..	430.3	77.7	1.97		1,737.	0.910
Sulphur trioxide........ .	491.4	83.8	2 02	0.262	2,105.	0.964
Trifluorotrichloroethane .	460.7					
Water........	647.3	218.2	0.91	0.232	1,400.	0.488
Xenon...................	290.	58.		0.276	1,057.	0.82

* Most of the data taken from *Bur. Standards Circ.* 279.   Hydrocarbon data from Edmister, *Ind. Eng. Chem.*, **30**, 353 (1938).
† Calculated from the critical pressure and temperature by

$$a = \frac{27}{64}\frac{R^2 T_c{}^2}{p_c}$$
$$b = \frac{RT_c}{8p_c}$$
$$R = 1.3145$$

‡ Critical point.
§ Cricondentherm point.
? Indicates doubtful values.

TABLE V.—CONVERSION FACTORS FOR a AND b OF VAN DER WAALS' EQUATION
(Original units: atm., cu. ft., °K., lb.-moles)

To change to	Multiply a by	Multiply b by
(1) atm., liters, °K., g.-moles.........	0.003896	0.0624
(2) atm. cc., °K., g.-moles............	3896.	62.4
(3) atm., cu. ft., °R., lb.-moles........	1.0	1.0
(4) lb./sq. in., cu. ft., °R., lb.-moles....	14.70	1.0

INDEX